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A Review

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THE ANALYSIS OF OIL SHALE WASTES:
A REVIEW

by

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This report summarizes the current status of methods for chemical analysis of oil shale effluents. It focuses on inadequacies in standard methods, adapted to oil shale analyses, particularly addressing needs of chemists, engineers, and biologists attempting to select an analytical scheme suitable for oil shale waste, including: sampling, analysis and quality assurance. Especially for the methods of questionable validity, the literature has been searched extensively so that alternate techniques could be included.

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FOREWORD

When energy and material resources are extracted, processed, converted and used, the related pollutional impacts on our environment, and even our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Before control technology can be judged to be efficient or not, reliable ways must be available to determine the compounds of interest. The material presented in this report summarizes the status of the analytical methodology available for the evaluation of samples derived from oil shale retorting processes. The information has been collected from the literature and oil shale researchers, and is aimed at the engineer or chemist who is faced with the everyday analytical problems of oil shale samples, or the evaluation of pollution control technologies. Further information can be obtained from the Energy Pollution Control Division, IERL-Cincinnati.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This report summarizes the current status of methods for chemical analysis of oil shale effluents. It focuses on inadequacies in standard methods, adapted to oil shale analysis, particularly addressing needs of chemists, engineers, and biologists attempting to select an analytical scheme suitable for oil shale waste, including sampling, analysis, and quality assurance. Especially for methods of questionable validity, the literature has been searched extensively so that alternate techniques could be included.

Elemental analysis of oil shale wastes is discussed with emphasis on determination of trace components. Methods considered include neutron activation analysis, X-ray fluorescence, inductively coupled plasma emission spectroscopy, traditional optical emission spectroscopy, spark source mass spectroscopy, and atomic absorption spectroscopy. The aim of this section is not to describe details of each procedure, but to outline principles of operation for each elemental technique to aid generalists in selecting an appropriate combination of techniques. In addition, operational and instrumental variations occurring among laboratories using the same technique are identified, and their effect on elemental coverage, detectability and accuracy is considered. Detection limits for each technique are included in the text, with emphasis on the effects of sample complexity. Less common variations of each of the elemental techniques are included also. As discussions and tables in Chapter 2 indicate, through using the proper combination of available instrumental methods, essentially every element in the periodic table can be determined not only in oil shale wastes, but in many other environmental samples as well.

In Chapter 3, characteristics of various retort waters are described, and reactions expected in retort waters during collection, storage, or chemical analysis are summarized. Applications of chromatographic, electrochemical, and wet chemical methods to the determination of inorganic compounds in water are also included.

Gas composition and problems of sampling and analyzing retort gases are discussed with special emphasis on the possibility of sample loss through reactions in the sampling train. Retort gas analyses in the literature are commonly found with inadequate explanations of methodology. An annotated bibliography has been provided to aid readers in literature surveys. Specific applications of spectrometric techniques to gas analysis are described, and details provided on the use of gas chromatography for sulfur compounds.

In the final chapter, availability of standard reference materials and data on sampling and preservation techniques are summarized, and quality assurance guidelines provided. As suggested throughout the report, standard methods of analysis and sampling, principally designed for routine testing, have not always been adequate for the analysis of oil shale wastes. Recommendations are made for developing alternate or improved techniques and standard reference materials.

This report was submitted in fulfillment of Contract No. 68-03-2791 by the Denver Research Institute under the sponsorship of the Environmental Protection Agency. This report covers the period April, 1979, to April, 1980, and work was completed as of June, 1980.

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1.0 INTRODUCTION

This report is written particularly for chemists and engineers working in the oil shale industry. It summarizes the current status of methods for the chemical analyses of oil shale effluents, and hopefully provides a valuable reference for those who must measure and control the effects of oil shale waste products on the environment. It is also recommended for enforcement and regulatory personnel, since neither emission limitations nor control technology requirements can be established without adequate measurement techniques.

This discussion includes spent and raw shale, process waters of various types, fuel gas produced by the retorting process (retort gas), and burned fuel gas. Methods are considered for the measurement of trace and minor elements, dissolved ions, organic compounds, sulfur and nitrogen species of environmental importance, and physical properties such as dissolved solids.

A comprehensive review of such a broad subject is clearly impossible in a single report. For this reason several annotated bibliographies are included as a guide to additional information.

It is well known that analytical methods which have been developed for relatively simple materials may be highly inaccurate when applied to more complex samples, often a great deal more inaccurate than the analyst expects. A classic description of this phenomenon is given by von Lehmden et al. (1974), who prepared homogenized samples of coal, fly ash, fuel oil, and gasoline for analysis in nine laboratories, each of which had analytical experience in the determination of trace elements in environmental samples. Of the 28 elements determined, agreement between laboratories was within an order of magnitude on all four samples for only seven elements!

Similar occurrences can be cited for oil shale wastes. For example, Fox et al. (1978) describe the difficulties of analyzing retort waters produced by burn number nine at the Rock Springs, Wyoming test site. Felix et al. (1977) and Farrier et al. (1977) indicate that the normal sample storage procedures are inadequate for retort waters. Difficulties in analyzing spent shale are described briefly by Wildeman and Meglen (1979) and Wildeman (1979). To the best of my knowledge, no such evaluations have been carried out for methods of gas analysis, presumably because of the difficulty in preparing and shipping simulated retort gases.

Methods for the analysis of oil shale effluents are obviously still under development, including efforts in our own laboratories, and I hope this report will serve as a basis for further discussion of such developments. In particular, it is my impression that analytical laboratories often develop minor modifications of standard methods "on the fly" in order to adapt them to difficult samples, and that such modifications are not normally published in the literature due to an unrelenting sample load. I welcome communications on such matters, especially since this report is to be followed by more detailed descriptions of analytical methods as they are developed.

A word is in order regarding the level of instrumentation which is required to perform the analyses described in this report. Since instrument availability varies greatly between laboratories, I have attempted to discuss analyses which can be performed with a minimum of equipment, as well as those which benefit by more expensive equipment. However, while not every laboratory owns a neutron generator, mass spectrometer, or electron accelerator, analyses performed by these instruments (as well as instrument time) can be obtained readily from commercial laboratories. As an example, neutron activation analysis, once principally restricted to the major nuclear research institutes, is now performed routinely by commercial laboratories. Gas chromatography/ mass spectrometry (GC/MS) systems have became a common feature in analytical services laboratories, much like atomic absorption spectrometers only a few years ago. It is thus a mistake to dismiss analytical methods which require such tools simply because of their high capital cost. At no time is this more important than when establishing values for standard materials, when a confirming (or contradictory) analysis by an independent method may be essential to the success or failure of an entire project.

The first chapter of this report discusses the elemental analysis of oil shale wastes of all types with emphasis on trace elements, and includes methods ranging from neutron activation and X-ray fluorescence to atomic absorption spectroscopy. Such methods naturally determine several elements simultaneously and are therefore approached by considering the entire periodic table, leaving the reader to select those elements most interesting to him. The objective of this chapter is not to extensively discuss individual methods, but rather to describe their synthesis into an analytical scheme suitable for oil shale wastes.

Chapter 3.0 discusses the analysis of wastewaters and leachates. The analysis of retort gas for those species which must be known in order to select and evaluate gas cleanup equipment is discussed in Chapter 4.0. The determination of criteria pollutants in flue gases (i.e., burned gases) is mentioned only briefly since instruments and techniques are already well developed for this purpose.

Discussions on preservation and standardization are included in the chapter on quality assurance (Chapter 5.0). Other facets of quality assurance, such as record keeping, instrument calibration, and statistical methods, are treated adequately elsewhere and are not repeated in this report.

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2.0 ELEMENTAL ANALYSIS: TOWARD AN INTEGRATED APPROACH

Anyone who has kept up to date on the developments in instrumental, multi-elemental methods for trace analysis has undoubtedly heard generalities such as "spark source mass spectroscopy determines more elements than any other technique but with the poorest precision," or "neutron activation analysis is the most accurate method for trace elements." Other common generalities include "atomic absorption spectroscopy is the most suitable technique when only a few elements are monitored," and "energy dispersive X-ray fluorescence is a fast and accurate method for elements heavier than Na in the periodic table."

In the context of a particular sample and a selected list of analytes, such statements may often be true. However, they are of no help whatsoever to a project chemist who must determine F, B, Mo, Cd, and Po in an oily wastewater, or to the wastewater engineer who must measure total N, S, and P in an industrial brine, or to the biologist who wants to measure Pb, Tl, and Si in lung tissue. In such cases, spark source mass spectroscopy may not detect the elements of interest, neutron activation may be inaccurate, and atomic absorption spectroscopy may be inapplicable. Clearly, the above generalities provide inadequate guidance for compiling analytical techniques for a specific problem.

Statements such as the above are often based on experience with commercial laboratories, or at least with analyses which are carried out in a fairly routine manner. As such, they overlook refinements and modifications which may dramatically improve the detectability or precision of a method. For example, in routine analysis, spark source mass spectroscopy is typically performed with a precision of approximately ± 40%, but under more carefully controlled conditions analyses of environmental materials have been completed to a precision of ± 4% (Morrison and

Colby, 1972). Similarly, B is not routinely detected by neutron activation in environmental samples. However, by using a variation of this technique in which one monitors γ-rays which are generated during (as opposed to after) neutron exposure, B can be measured accurately in fly ash, coal, and other complex samples (Failey et al., 1979). Awareness of such modifications and variations can often determine the success or failure of a program. Especially when establishing concentrations in a critical chemical standard, the extra costs associated with such non-routine methods can be readily justified.

Often the principal investigator or project manager who selects the analytical techniques is not the one who physically completes the analysis. Rather, persons who are experts in individual techniques may analyze the sample, while the principal investigator hopes to coordinate the analytical efforts of several laboratories. Coordinating and integrating trace techniques into a overall analytical scheme capable of achieving project goals has become a specialty in itself, whose practitioners are most expert not in neutron activation, X-ray fluorescence, or atomic absorption spectroscopy, but rather in orchestrating various analytical techniques for the objective at hand.

The purpose of this chapter is therefore to aid chemists, engineers, and biologists in selecting the trace analytical methods most appropriate for their programs. The techniques discussed include nuclear activation methods, X-ray fluorescence, inductively coupled plasma spectroscopy, optical emissions spectroscopy, spark source mass spectroscopy, and atomic absorption spectroscopy. Obviously, each technique cannot be discussed in detail here. Rather, only the most basic principles of operation and such figures of merit as detectability, linear range, precision, accuracy, elemental coverage and interferences are discussed. In addition, some of the less common modifications are referenced. Despite the necessary limitations in the scope of this report, the information it provides should be helpful in selecting successful analytical schemes.

It must be emphasized, though, that because each technique included here is constantly being refined, the instrument expert should be included in discussions early in the development of an analytical scheme. The goal of the following pages is therefore to facilitate such discussions by providing the generalist with an elementary basis for comparing each technique, and by alerting the generalist to some of the less routine methods which are often available to those who ask for them.

Since current techniques are inherently multi-elemental, this chapter includes essentially every element in the periodic table. Exceptions include the inert gases He-Xe, which are normally determined by gas chromatography, and the synthetically prepared elements Tc and Pm.

When faced with a new analytical problem, the common and justifiable tendency of most chemists is to try first those instruments which they have at hand in the laboratory. However, to limit themselves to this approach is to overlook the many instrumental services which can be obtained from commercial laboratories. These include all the major techniques such as X-ray fluorescence, spark source mass spectroscopy, neutron activation, inductively coupled plasma spectroscopy, optical emission spectroscopy, and atomic absorption spectroscopy, as well as some less common techniques such as photon and charged particle activation.

This chapter should perhaps be sub-titled "How a Complete Novice Can Determine Every Element in the Periodic Table with No Instruments." The facetious solution would actually be to hire the proper experts along with their instruments. However, I do hope that the following material can help generalists achieve their analytical goals as efficiently as possible.

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Morrison, G.H. and B.N. Colby. 1972. Precision of Electrical Detection Measurement of Powdered Samples in Spark Source Mass Spectrometry. Anal. Chem. 44:1206.

2.1 Significance of Trace Elements in Oil Shale Retorting

The potential impact of trace elements emissions from oil shale retorting has been much discussed in the literature and therefore will be only briefly summarized here. Data on trace elements associated with oil shale were reviewed in 1977 in a joint effort by TRW and the Denver Research Institute (TRW/DRI, 1977). Authors of similar reviews on the role of trace elements include the Energy Research and Development Administration (1975), the National Research Council (1977), Chappell et al. (1978), Fox (1979[a]), and the U.S. Environmental Protection Agency (in press).

The source and fate of trace elements in laboratory-scale retorting experiments are described by Fox (1977[a]), Fox et al. (1978, 1979), Wildeman and Meglen (1977), and Shendrikar and Faudel (1978). Trace elements associated with pilot scale retorting have not been extensively studied, and to the best of my knowledge only two reports appear in the literature: Fruchter et al. (1979) and Cotter et al. (1978), both of whom studied the Paraho retort at Rifle. The geological distribution of trace elements in the western oil shale areas has been described by Donnel and Shaw (1977) and Desborough and Pitman (1976). Additional references are included in a bibliography at the end of this chapter.

Particularly lacking in the literature are measurements of trace elements in pilot scale (or larger) retorting operations, discussions of the role of control technology in minimizing emissions of trace elements, and the chemical form in which trace elements occur.

Interest in trace elements arises because of the general phenomenon of partitioning that occurs during the combustion of solid fuels. For example, Wallace (1974) and Davison et al. (1974) have shown that in a coal fired power plant the elements Pb, Te, Sb, Cd, Se, As, Zn, Ni, Cr, and S are at least ten times more concentrated in the smallest fly ash particles than in the bulk coal ash. A study by Radian Corporation has shown that the elements Sb, As, B, Cd, Cl, Ca, Co, F, Pb, Mg, Hg, Mo, Ni, Se, Ag, S, U, V, and Zn are at least three times more concentrated in the entrained fly ash particles leaving the stack than in the bulk coal ash, and that 80-96% of the Hg in the coal escapes with the flue gas.

The partitioning of trace elements during combustion apparently occurs by volatilization during the burning or roasting process. The interest in oil shale arises because of the large mass of ore which must be retorted per unit of energy produced. (The heat content of 30 gal/ton oil shale is approximately 2800 Btu/lb, compared to 10,000 Btu/lb for coal.) Fortunately, the partitioning of trace elements during oil shale retorting is much less pronounced than in coal combustion (Fox et al., 1977), although considerable interest exists in the trace elements Hg, As, Cd, and Se and the minor elements N and S.

Particular attention has been given to elements which are partitioned into the gas phase since potential inhalation of trace elements represents a route of direct human exposure. In laboratory experiments which were designed to simulate in situ technology, Fox (1978) has observed Hg partitioning into the gas phase in amounts varying from negligible to 86%. Based on mass balance studies, Fox (1979a) also suggested the possibility of Cd in the retort gas, although no direct measurements of Cd in the gas were obtained at the Paraho semi-works plant. Fruchter et al. (1979) also detected Hg and As in the retort gas corresponding to 23% and 0.08% respectively of the total element processed.

Additional measurements of trace elements in the gas stream are likely on full scale plants as they are built. Also, since the effect of control equipment on trace elements has not yet been experimentally determined, methods must be available for measuring the efficiency of control equipment for elements such as Hg, Cd, and As. For example, does the Stretford process, which is designed to remove H_2S, coincidentally remove Hg? In addition, the behavior of trace metals in control equipment would be easier to predict if methods for chemical speciation were readily available: Hg which is present as elemental Hg gas would be removed differently in a Stretford unit than would Hg present as $Hg(CH_3)_2$ or as small particles.

Arsenic in raw shale oil has attracted considerable attention because it is significantly elevated over levels found in petroleum oils (TRW/DRI, 1977). The elements N, S, Hg, Se, Sb, and Cd in oil shale have also attracted attention (Fruchter et al., 1977).

Future measurements of trace metals in shale oil will likely require the following: First, most previous measurements have been concerned with bench or pilot scale operations. Element partitioning in a full scale retort may differ and need to be investigated. Second, distillation and refining of shale oil may remove many trace elements (Shaw, 1978; TRW/DRI, 1977), a possibility which should be investigated further. As for trace elements in retort gas, methods of analysis which are capable of chemical speciation would aid in predicting the fate (and effect) of trace elements during refining, distillation, and use.

Present development plans for oil shale call for zero discharge of process waters, as all process water will either be consumed in the retorting process or used for spent shale moistening. This processing method requires extensive water treatment for internal reuse, and includes the use of low grade waters to moisten the spent shale (Nevens et al., 1979). Future analyses of process water for trace and minor elements such as N and P may therefore be justified because of their effect on water treatment.

Runoff and leachates from spent shale and other solid wastes constitute a wastewater distinctly different from retort water. The elements B, F, Mo, and Se have been observed in leachates and will likely be monitored in the future because of their phytotoxic effect. In addition to elements having a direct environmental effect, any species that is particularly enriched in leachates as compared to undisturbed groundwaters is valuable as a "tracer" for hydrological studies of groundwater movement near abandoned retorts. Species which are soluble under basic, oxidizing conditions, such as Mo, Se, Te, Cr, and U, could be useful for tracing purposes (GE/TEMPO, 1979).

Unlike process waters, excess mine water may be discharged to surface streams. Current permits (Permit No. CO-0 345045) restrict the amount of B and F which may be discharged, so that these elements may be monitored in future discharge waters.

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2.2 Activation Analysis

In its most general sense, activation analysis refers to any of a number of methods which rely on activation of the subject nucleus by photons, neutrons, or other particles, and detection of the various decay products. A summary of various activation schemes, classified by the exciting and detected medium, is shown in Table 2.1. Some of these methods are sufficiently common to warrant abbreviations, such as INAA for instrumental neutron activation analysis, which will be used subsequently throughout this text.

Even though the terms in Table 2.1 are more specific than "activation analysis," they nevertheless still refer to generic types of analyses and not the exact procedures. For example, the activation step may be accomplished by a steady flux of thermal neutrons from a reactor, 14-MeV neutrons from a neutron generator, or a pulse of neutrons $\sim 10^5$ times more intense than a reactor normally produces. Each of these options greatly affects the success of final analysis.

In Table 2.1 radiochemical neutron activation analysis (RNAA) refers to procedures which require a chemical separation prior to counting. RNAA is listed in two columns since either γ-rays or β particles are commonly counted. The term "instrumental" in this table is somewhat inappropriate since essentially all the activation methods require instruments. Nevertheless, I follow common usage in applying this term to analyses performed with a high resolution Ge(Li) detector. X-ray fluorescence (XRF) and particle induced X-ray emission (PIXE) both rely on the behaviors of inner-shell electrons and are therefore not normally considered activation methods. They are included in Table 2.1 not only to show their relationship to activation methods but more importantly, because they require instruments which are quite similar to those required by other activation methods.

TABLE 2.1. ACTIVATION METHODS FOR ENVIRONMENTAL SAMPLES
Common acronyms are included when appropriate.

EXCITATION	DETECTION			
	Prompt γ-rays or X-rays	γ-rays from the decay of radioactive products	neutrons	other particles
Neutrons	Prompt γ-ray Activation Analysis (PGAA)	Instrumental neutron activation analysis (INAA), Radiochemical neutron activation analysis (RNAA)	Delayed neutron counting	Radiochemical neutron activation analysis (RNAA), particle rack etching
γ-rays or X-rays	X-ray Fluorescence (XRF)	Instrumental photon activation analysis (IPAA)		
Other Particles	Particle Induced X-ray Emission (PIXE), Particle induced γ-ray Analysis	particle induced activation analysis		

Of the methods shown in Table 2.1, neutron activation is established as a routine and widely used analytical tool and will therefore be discussed in greater detail.

2.2.1 Neutron Activation Analysis

The literature on neutron activation analysis is sizeable. Historically, the number of papers published each year on activation analysis has doubled every three years and stood at over 500 papers for the year 1970. Here I summarize only those features which are most essential to the non-practioner, who may gain access to neutron activation services through commercial laboratories, and refer the reader to the many texts for more in-depth discussions (Coomber, 1975; West, 1976; Guinn, 1971).

Neutron activation analysis is truly a multi-elemental technique which has been used to determine every element lighter than Po (though not at one time) with the exception of B, Be, C, H, He-4, and Li. Up to 45 elements have occasionally been determined at one time, but a routine assay may often report six or less successful determinations. (Bowen, 1975). What, then, are the variables which so greatly affect the success of neutron activation?

Neutron activation begins when a nucleus absorbs a neutron to produce a radioactive isotope. In shorthand this reaction can be written as $^{27}\mathrm{Al}(n,\gamma)^{28}\mathrm{Al}$, which means that Al-27 absorbs one neutron and emits γ radiation to produce the radioactive isotope Al-28. The sample is removed from the neutron source, allowed to decay for a measured period, and is then counted. Differences in the means of neutron exposure, the method of detection, and decay times distinguish several analytical schemes known generically as neutron activation. More importantly to the reader, these differences may distinguish one commercial laboratory from another and will change detectabilities by orders of magnitude.

Basic Principles

When an element is exposed to a source of neutrons or activating particles for a time t_e and then allowed to decay for a time t_d, its activity is given by

$$A = \frac{\phi\sigma W f}{M}\,(1-e^{-\lambda t_e})\,e^{-\lambda t_d}\,(6.023\times10^{23}) \qquad (2.1)$$

where ϕ = neutron flux ($cm^{-2}\ sec^{-1}$)
σ = absorption cross section (cm^2)
M = gram atomic weight of isotope (g)
W = weight of element in sample (g)
f = isotopic abundance
λ = decay constant = $0.693/t_{\frac{1}{2}}$

In the absence of complicating factors (such as the presence of other elements!) good sensitivities are therefore favored by a high neutron cross section, high neutron flux, a high-isotopic abundance, and a low molecular weight. t_e should be $\geqq t_{\frac{1}{2}}$ and t_d, as short as possible.

In practice t_e is often limited to 24 hours because of costs and the impatience of the practitioner. For short-lived isotopes, the minimum value of t_d is limited instrumentally by the requirement of retrieving the sample from the interior of a reactor before counting. For long-lived isotopes the minimum value of t_d may be days or months in order to allow short-lived interferences to decay.

In neutron activation the most common irradiation product occurs through absorption of a single neutron: $^{75}As(n,\gamma)^{76}As$. However, other reactions, referred to as fast neutron reactions, are also possible: $^{16}O(n,p)^{16}N$, $^{14}N(n,-2n)^{13}N$, $^{35}Cl(n,d)^{32}p$, $^{27}Al(n,d)^{24}Na$ to name a few. In some cases fast neutron reactions generate unwanted interferences, while in other situations they represent a valuable analytical probe, especially when the fast neutron product is readily detected while the

(n,γ) product is non-radioactive. In any case their importance cannot be overlooked. The occurrence of fast neutron reactions depends largely on the energy distribution of the incident neutrons, and under irradiation with thermal neutrons they are often, but not always, unimportant. The design and selection of neutron sources thus centers on achieving the desired neutron energy distribution as well as maximum neutron flux.

Neutron Sources and Sample Activation

Neutron sources are distinguished by their flux density and energy distribution. The most common neutron source is a nuclear reactor where flux densities are typically in the range 10^{11} - 10^{13} cm^{-2} sec^{-1}. In a reactor, neutron energies vary from ~0.025 ev to 25 MeV. The energy distribution varies from almost entirely thermal neutrons (~0.025 ev), in regions occupied by the moderator, to approximately equal numbers of fast (> 1 MeV) and thermal neutrons near the fuel rods (Bowen, 1975).

The latter distribution is important because most elements are activated most efficiently by thermal neutrons and reactions caused by fast or epithermal (0.2 - 1000 ev) neutrons may generate interferences and side reactions. For example, ^{32}P produced by the fast neutron reaction $^{32}S(n,p)$ ^{32}P interferes with the determination of P by the thermal-neutron $^{31}P(n,\gamma)^{32}P$ reaction. Table 2.2 includes other such fast-neutron interferences which may be important when, for example, V is determined in a Cr ore or when Na is measured in an Al alloy.

The ratio of fast to thermal neutrons is often greatly increased by enclosing the exposure chamber with a Cd sheath which preferentially absorbs thermal neutrons. By exposing samples with and without the Cd sheath, products from fast-neutron and slow-neutron reactions can be distinguished since the abundance of fast neutron products will change less than the abundance of thermal neutron products.

TABLE 2.2. INTERFERENCES IN NEUTRON ACTIVATION CAUSED BY FAST-NEUTRON REACTIONS

Analyte	Interfering Reactions
P via $^{31}P(n,\gamma)^{32}P$	$^{32}S(n,p)^{32}B$, $^{35}Cl(n,a)^{32}P$
Na via $^{23}Na(n,\gamma)^{24}Na$	$^{27}Al(n,\alpha)^{24}Na$
Al via $^{27}Al(n,\gamma)^{28}Al$	$^{28}Si(n,p)^{28}Al$, $^{31}P(n,\alpha)^{28}Al$
V via $^{51}V(n,\gamma)^{52}V$	$^{52}Cr(n,p)^{52}V$

In addition, certain elements are determined preferentially by activation with fast neutrons, either because they are more readily activated by fast neutrons or because the product is more readily detected. Examples include the activation of O by fast neutrons according to the reaction $^{16}O(n,p)^{16}N$ and the fast-neutron activation of Tl to form an easily detected γ emitter rather than the β emitter produced by the thermal neutron (n,γ) reaction. The elements N, O, F, Si, P, Cr, Ni, Fe, Rb, Se, Tl, and Pb can be determined as sensitively with fast neutrons as with thermal neutrons; however, most elements are determined preferentially with thermal neutrons because thermal neutron cross sections are typically 1000 times larger than fast neutron cross sections (Guinn, 1969).

Reactors which have been specially designed (e.g. TRIGA reactors) can be pulsed to a flux density of 10^{16} - 10^{17} cm^{-2} sec^{-1} for periods of 5 - 30 msec. This design feature is valuable in the measurement of short lived isotopes because of the $\exp(-\lambda t_e)$ term in equation 2.1, provided that samples can be counted soon enough after exposure. In practice, the fastest pneumatic transfer tubes move the sample from reactor to counter in about 0.5 sec. under such conditions, and the activity of short lived isotopes is enhanced by a factor of about $70/t_{\frac{1}{2}}$, where $t_{\frac{1}{2}}$ is the half-life in seconds. Elements which have been measured accordingly with pulsed reactors include F, Pb, Li, B, Se, O, and N (Guinn, 1969; Guinn, 1971).

In addition to nuclear reactors, neutron generators and radioactive isotopes such as ^{252}Cf and Am/Be also serve as neutron sources. Isotope sources are normally quite weak (10^5 - 10^8 cm^{-2} sec^{-1}) and range in energy from 0.024 - 4.0 MeV (Bowen, 1975). The low neutron flux of isotope sources limits their application to the determination of major elements for industrial process control (e.g. F in fluorite), or to analyses in inaccessible locations, and they will not be treated further here.

On the other hand, neutron generators are valuable as a source of fast neutrons. The most common neutron generator operates by bombarding a Zr^{3}H target with deuterons whereupon 14 MeV neutrons are produced by the reaction

$$^{2}H + {}^{3}H \rightarrow {}^{4}He + n \qquad (2.2)$$

Neutron fluxes are in the range of 10^8 - 10^{11} cm^{-2} sec^{-1} (Bowen, 1975). O is determined quite commonly using the $^{16}O(n,p)^{16}N$ reaction, and some researchers have suggested that 14 MeV neutrons could be used in measuring N in oils, and A, Fe, Mg, and Si in rocks. Perdyin (1967) describes the utility of 14-MeV activation analysis for 47 elements. The elements most often determined with 14 MeV neutrons include O, F, Mg, Al, Si, P, Fe, Cu, and Zn (Cornelius et al., 1976).

Radiation Detectors

In theory, the activated products can be detected by γ radiation, α or β particles, or even fission fragments. In practice, neutron activation is completed almost entirely with γ-ray detection using semiconductor detectors.

β detection is important only in radiochemical neutron activation because the sample must normally be dissolved and separated from other interfering species. Nevertheless, when the radionuclide is essentially only a β emitter (e.g. ^{210}Bi), or when it is detected more readily by β emission, the better detectability obtained by β counting may be worth the extra effort. Here I only wish to alert the reader to these alternatives and to refer him to the chapters by Cunningham (1975) for a more in-depth discussion of particle detectors.

With the exceptions mentioned in the last paragraph, neutron activation analysis is currently performed almost exclusively with semiconductor Ge(Li) and Si(Li) detectors, and only rarely with NaI(Tl) scintillation counters. Resolution in semi-conductor detectors is normally sufficient to eliminate the need for any chemical separation so that INAA, originally implying no chemical separation, has become synonymous with the use of Ge(Li) or Si(Li) detectors. However, this class of detectors varies markedly in signal-to-noise ratio, resolution, maximum counting rates, and efficiency, and the wise purchaser should be aware of these differences.

When a γ-ray passes through a Ge(Li) detector, it produces a series of electrons and holes which are collected by an amplifier, with the collected charge proportional to the energy of the γ-ray, E_γ. The resolution of a semiconductor detector therefore varies as

$$R = \sqrt{N_e^2 + aE_\gamma^2} \tag{2.3}$$

where N_e = the contribution of electronic noise

a = a factor which depends on the energy required per electron/hole pair

Here, the aE_γ^2 term arises because of the statistical nature of charge generation. For a given detector, if R is known at a few points, it is known throughout the spectrum. Under typical conditions the resolution (FWHM) of the Ge and Si detectors are approximately 1.3 and 2.0 keV respectively at E_γ = 1.0 MeV although this difference increases at lower energies (Dams et al., 1976).

Counting rates up to 10 kHz are readily available, although resolution degrades as counting rates increase. Because the detector and amplifier must count and sort all photons simultaneously, the maximum counting rate implies that the presence of a highly radioactive isotope limits the detectability of other isotopes. Because of the counting rate limitation, often only the most active isotopes are detected during each counting period.

Efficiency of the detector increases with size and atomic number of the detector material, being best for the Na(I) scintillation detector and poorest for the Si(Li) semi-conductor, and decreases with increasing photon energy. Unfortunately, resolution degrades with larger detector size. Absolute detection efficiencies, including geometry effects, vary from 10^{-1} to 10^{-4}.

A continuous background which increases toward lower energies is one of the most noticeable features of a γ-ray spectrum. This background arises principally from photons which are scattered elastically (Compton scattering) from the detector and which therefore deposit only a variable fraction of their total energy. This background ultimately determines the lower detectable limit and is of obvious concern. (Some laboratories have available anti-coincidence counters which detect the scattered photons and discount any "coincident" pulses, thereby improving background count rates and detectability for most elements). The ratio of peak height to the lower energy Compton background varies from 30:1 to 10:1, depending on the detector. Clearly, the detectability of a given peak depends largely on the presence of higher energy radionuclides in the sample.

In the region below ~500 keV this problem is sometimes addressed by using smaller Ge(Li) detectors or Si(Li) detectors known as Low Energy Photon Detectors (LEPD). Both are less efficient than the normal size Ge(Li) detectors in the region over a few hundred keV, but may be of comparable efficiency below that region. The Compton background in the low-energy region is thereby reduced and the signal-to-noise ratio may be improved 10-30 fold. Another factor which improves the signal-to-noise ratio for the LEPD is its better resolution in the low energy section of the spectrum.

Because of the above mentioned difficulties in measuring many elements during a single counting period, multiple counting periods and exposure periods are common. Such decay schemes vary from laboratory to laboratory and are designed to minimize the effects of Compton scattering and count rate limitations. The effect of varying decay schemes is illustrated by Ondov et al. (1975) who describe the decay and exposure schedules employed by several major laboratories and compare their successes in analyzing coal and fly ash.

Table 2.3 summarizes several factors which determine the effectiveness of neutron activation, as discussed in this section. With these physical principles described, a few examples can now be considered.

Examples

One approach to judging whether NAA is appropriate for one's sample is to simply survey the literature to determine whether similar samples have been previously analyzed successfully for the elements of interest. For this reason I have assembled the results of NAA for various environmental samples in Table 2.4. It is likely that those elements which were determined successfully by every author in every matrix in Table 2.3 will likely be successfully determined in the reader's (similar) sample (e.g. Sb, Br, Se, As, Sc, Cl, Al, and Na). But for the other elements, why is there such a wide variation in successful measurement?

The natural differences in concentrations in the various samples are one obvious explanation. La is probably higher in oil shale than in shale oil and could therefore be more readily detected. This interpretation is rather limited and does not explain, for example, why Fox

TABLE 2.3. FACTORS DETERMINING THE EFFECTIVENESS OF NEUTRON ACTIVATION

Most factors listed below, with the exception of physical properties of the nucleus, vary between laboratories and samples.

Neutron Source

- neutron flux
- energy distribution of neutrons
- pulsed or constant source
- reactor source
- isotope source
- neutron generator

Irradiation Scheme

- exposure time
- decay time
- minimum time required to remove sample from source to counter
- chemical separation of radioisotope
- chemical removal of an interfering element

Detection

- type of radiation - γ,β, prompt or delayed emissions
- Ge(Li) detector - size, efficiency, resolution
- maximum counting rate
- Compton ratio
- Si(Li)
- LEPD
- NaI(Tl) - scintillation

Other

- neutron cross section
- gram atomic weight
- isotopic abundance
- half life
- other elements with similar or longer half lives, especially if E_γ (analyte) $\leq E_\gamma$ (other element)

TABLE 2.4. THE RESULTS OF NEUTRON ACTIVATION ANALYSIS FOR VARIOUS ENVIRONMENTAL MATERIALS. Concentrations are in μg/g unless otherwise noted.

	Fruchter et al. (1979)			Ondov et al. (1975)[d]		Dams et al. (1975)	Fox et al. (1978)	USGS Standard Rocks[g]
	Oil Shale	Shale Oil	Retort Water	NBS Coal	NBS Fly Ash	Airborne Particles	Retort Water (μg/ml)	Flanagan (1976)
H								
Li								[12.7] [a]
Be								
B								
C								
N								
O						28.7% [e]		44.9% [e]
F						0.24 [h]		800
Na	1.68%	3.43	115	399	3400	0.96%	4210	2.84%
Mg		14	460	(0.16%)	(1.5%)	0.78%		2.21%
Al	3.89%	10.3	<0.4	1.78%	13.2%	1.6%	19.1	7.73%
Si					(21.%) [b]	6.8% [e]		25.5%
P								1500 [a]
S		0.73%	3.9%			4.0%		
Cl		0.6	36	970	(42)	1.2%	793	99
K	1.69%		38	0.27%	1.6%	0.69%		0.83%
Ca	10.4%			0.41%,0.47[b]%	(4.2%),5.3% [b]	3.8%		4.98%
Sc	5.77	0.0031		3.7	27	2.87	0.00145	0.36
Ti	0.18			960,890 [b]	7300,7300 [b]	2500		1.33%
V	86	0.190	0.045	37	251	2020		375
Cr	36.7	<0.03	<0.06	19.7	130	195		23
Mn	312	0.15	0.13	41	509	1300		1465
Fe	2.08%	44	<3	0.86%	6.2	32,500		4.55%
Co	9.0	1.05	0.32	5.6	41.2	17		30
Ni	23.0	2.58	0.530	(16)	(105),92 [b]	1500		38
Cu		<0.5	<1			700		17 [a]
Zn	67	0.46	0.44	(30)	216 [b]	7100		131 [a]
Ga						10		20 [a]
Ge								1.7 [a]

TABLE 2.4 (continued)

	Fruchter et al. (1979)			Ondov et al. (1975)[d]		Dams et al. (1975)	Fox et al. (1978)	USGS Standard Rocks[g]
	Oil Shale	Shale Oil	Retort Water	NBS Coal	NBS Fly Ash	Airborne Particles	Retort Water (μg/ml)	Flanagan (1976)
As	48	28.0	5.63	5.7,8.2 [b]	60,61.5 [b]	85	0.84	0.84 [a]
Se	2.1	0.91	9.5	3.1	10.3	12	0.38	0.105
Br	0.57	<0.06	<0.05	20	(12)	700	2.07	0.24 [a]
Rb	74.9	0.04	0.150	20	124,126 [b]			44 [a]
Sr	674		1.10	(170)	(1900)			318
Y					(62) [b]			36 [a]
Zr					301 [b]			272
Nb								
Mo						30		1.0 [a]
Ru								[2.5]
Rh								
Pd								12 [a]
Ag				(0.06)		12.4		0.031 [a]
Cd	0.64 [a]							0.099 [a]
In				(0.20)	(0.32)	0.40		0.08
Sn								1.5 [a]
Sb	2.09	0.035	0.020	4.3	7.8,7.0 [b]	257	1.81	0.8
Te								<1
I					2.9 [b]	14.4		[0.038]
Cs	3.8			1.14	7.9	2.15		1.4
Ba	483			330	2700	9.70		655
La	20.6			11.3	82	75		28
Ce	43			(20.4)	(156)	138		43 [a]
Pr								7.3 [a]
Nd	20.4							30.1
Sm	3.1			1.83	13.8	7.5		5.7
Eu	0.60			0.38	2.9	0.45		1.95
Gd								5 [a]
Tb	0.37			(0.22)	1.7			1.1

TABLE 2.4 (continued)

	Fruchter et al. (1979)			Ondov et al. (1975)[d]		Dams et al. (1975)	Fox et al. (1978)	USGS
	Oil Shale	Shale Oil	Retort Water	NBS Coal	NBS Fly Ash	Airborne Particles	Retort Water (μg/ml)	Standard Rocks[g] Flanagan (1976)
Dy	2.4					2.3		6
Ho	0.67							1.15
Er								3.5
Tm								0.6
Yb	1.26			(0.7)	(5.1)			3.5
Lu	0.28			(0.14)	(1.0)	0.20		1.0 [a]
Hf	1.75			0.95	7.9	1.0		4.1
Ta	0.55			0.21	1.64			1.2
W				(0.87)	(5.7)	17		0.44 [a]
Re								0.00083
Os								<0.0001 [a]
Ir						<35		0.14 [a]
Pt								2.3 [a]
Au						2.5		0.057 [a]
Hg						21.6		4 [a]
Tl								0.278 [a]
Pb					75 [b]			
Bi								0.0432 [a]
Po								
At								
Fr								
Ra								0.56×10^{-6} [f]
Ac								
Th	6.33	0.008		3.0,3.4 [c]	23.5,26.2 [c]	2.8	<0.024	9.0
Pa								
U	4.2		<0.10	1.41 [c]	12.0 [c]	1.15 [h]	<0.91	1.8
Total by activation method	36	17	15	36	40	43	8	67
No. Irradiations	2	2	2	1-3	1-3	6	2	
No. Counts	4	4	4	1-4	1-4	10	5	

TABLE 2.4 (continued)

flux (cm^{-2} sec^{-1})	$6x10^{12}$	$6x10^{12}$	$6x10^{12}$	10^{12}-10^{13}	10^{12}-10^{13}	$2x10^{12}$	$2x10^{12}$

[a] Radiochemical neutron activation analysis

[b] Determined by instrumental photon activation analysis

[c] Determined by direct γ spectroscopy on a sample of 100 g

[d] Parentheses indicate that the element was not reported by two or more of the four laboratories performing neutron activation

[e] Used fast (14 MeV)

[f] Radar counting determined by

[g] All values refer to standard rock BCR-1, except those values in parentheses which refer to other standard rocks listed by Flanagan (1976)

[h] Determined with epithermal neutrons (Cd shielding)

reports <2000 μg/g of Zr in retort water and Flanagan, 272 μg/g in standard rocks.

Of more importance are the authors' objectives in their studies, and this deserves a few words. Fruchter et al. (1979) attempted to measure the element mass balances in an oil shale retort, not to demonstrate the power of INAA. Other elements which were not measured by INAA were detected by X-ray fluorescence or atomic absorption spectroscopy, and INAA was meant to complement these other techniques.

Ondov et al. (1975) were attempting to establish standard references values for coal and fly ash samples by using the round-robin approach with four laboratories. With the exception of the IPAA analyses carried out by the Maryland group, most laboratories used a routine protocol employing thermal neutron exposure in a reactor.

As can be seen, approximately 1/3 of the detected elements were reported by only one or two of the laboratories, indicating the importance of the exact protocol and analytical conditions in the success of INAA.

Dams et al. (1975) were attempting to obtain a complete elemental analysis of airborne particulate matter by whatever means were available, including combustion and colorimetric methods. While not attempting to stretch activation methods to their limits, they did place more emphasis than usual on nuclear methods, especially for the measurement of O, F, Se, and U. The variety of irradiations, decay schemes, and detectors which were required by Dams is illustrated in Table 2.5.

Fox et al. (1978), like Ondov, were attempting to establish reference values for an oil shale process water by participating in a round-robin. Unlike the data for Ondov, which is a composite from several INAA analyses, the data shown for Fox includes only the results of a single analysis, which is more indicative of what could be expected under normal procedures. Fox's data provides a valuable list of detection limits for

TABLE 2.5. SUMMARY OF IRRADIATION AND COUNTING SCHEME USED BY DAMS et al. (1975)

Neutron energy	Exposure time	Decay times	Elements	Detector
Thermal (from reactor)	5 min.	3 min.	Na, Mg, Al, Cl, S,	50 cm^3 Ge(Li)
		15 min.	K, Ca, Sc, Ti, V,	
			Cr, Mn, Fe, Co,	
"	7 hr.	1 day	Ni, Cu, Zn, Ga,	
		5-7 days	As, Sc, Br, Mo, Ag,	
		20 days	In, Sb, I Cs, Ba,	
			La, Ce, Eu, Sm,	
			Dy, Lu, W, Au, Hg, Th	
"	18 sec.	10 sec.	F	"
epithermal (Cd sheath)	30 sec.	25 sec.	F, Sc, Se, Ag, Hg	"
"	5 min.	15 min.	U	Low Energy Photo Detector (i.e. high resolution, low efficiency Ge detector)
14 MeV	15 sec.	5 sec.	O	Na (I)
		75 sec.	Si	Na (I)

oil shale retort wastewaters and illustrates what could be expected from a routine protocol.

The data by Flanagan (1976) represents efforts to standardize a geological reference material. These samples are some of the most thoroughly analyzed in the literature: a number of laboratories determined as many elements as possible using multiple techniques. Flanagan's data includes numbers from several laboratories using a variety of INAA and RCAA methods, and therefore represents the most that can reasonably be expected with neutron activation techniques (available through 1972). In particular, it should be noted that approximately 1/3 of the elements could be measured only with RCAA and not INAA.

Detection Limits

Of more fundamental value in explaining Table 2.4 are estimates of detection limits, interferences, and other physical data such as those presented in Table 2.6. Activation products with half lives $\leqq 30$ sec. (column 3, Table 2.6) present special handling problems which not every laboratory is equipped for. Activation products with $t_{\frac{1}{2}} < 30$ sec. include ^{8}Li, ^{12}B, ^{16}N, ^{19}O, ^{20}F, ^{77m}Y, ^{110m}Ag, ^{179m}Hf, and ^{207m}Pb, although other isotopes are available for Se, Y, Ag and Hf.

The fourth column indicates photopeak energies which are most often used, although other, less sensitive lines are available when spectral interferences are a problem. Note that several isotopes emit no γ radiation, so their detection by INAA is not possible. Column 4 also indicates which species could benefit from the availability of a Low Energy Photon Detector (LEPD).

The interferences in column 5 are those most likely to be encountered in environmental samples and by no means constitute a comprehensive list.

TABLE 2.6. DETECTION LIMITS AND ESSENTIAL PHYSICAL DATA FOR THERMAL NEUTRON ACTIVATION ANALYSIS. The detection limits are typical of those obtained by exposing the sample in a reactor and detecting the omitted radiation with a Ge(Li) detector of nominal 50 cm^3 active volume. Detection limits may vary by orders of magnitude, but can be anticipated based on sample type, irradiation scheme, and other factors.

					Calculated Detection Limits		Experimental Detection Limits				
	Radio-nuclide	$t_{1/2}$	Photopeak energy (MeV)	Possible interference	INAA (μg/g)	β counting (μg)	Retort Water Fox et al. (1978) (μg/ml)	Shale Oil Kovar (1979) (μg/g)	Sea Water Kovar (1979) (μg/g)	Limestone Kovar (1979) (μg/g)	Comments
H	^{3}H	12.3 y	-		-	1.0 g					
Li	^{8}Li	0.85 sec	-	^{8}Li→2α	-	-					
Be	^{10}Be	2.7x10^{6} y	-		-	300 g					
B	^{12}B	0.02 sec	-		-	-					
C	^{14}C	5370 y	-	^{14}N(n,p)^{14}C	-	300 g					
N*	^{16}N	7.13 sec	2.75	^{16}O(n,p)^{16}N	400 g	-					
O*	^{19}O	26.8 sec	0.197		0.1 g	-					
F*	^{20}F	11.6 sec	1.632	^{28}A(1.78)	200		3,000				$t_{1/2}$ Small, Al interference
Na	^{24}Na	15.0 hr	1.369	^{27}Al(n,α)^{24}Na, ^{24}Mg(n,p)^{24}Na	0.9	0.04		0.1	D	0.1	
Mg	^{27}Mg	9.46 m	0.843	^{27}Al(n,p)^{27}Mg; Mn(0.847)	50	4	500	700	800,000		interferences
Al	^{28}Al	2.31 m	1.780	^{28}Si(n,p)^{28}Al	1	2					
Si*	^{31}Si	2.62 m	1.264		20,000	0.9	4,000	43,000			
P*	^{32}P	14.3 d		^{32}S(n,p)^{32}P; ^{35}Cl(n,α)^{32}P	-	2	2,000				use (n,p) reaction upper limit
S	^{35}S	87.9 d	-	^{35}Cl(n,p)^{35}S	-	200					
	^{37}S	5.07 m	3.09		20,000	1,000	30,000				
Cl	^{38}Cl	3.73 m	1.60		20	0.2		0.2	D	1,500	
K	^{42}K	12.4 hr	1.524		40	0.2	2,000	7	5,000	7	High Compton from Na (2.75)
Ca	^{49}Ca	8.8 m	3.10		500	10	400	1,000	1,300	300	
Sc	^{46}Sc	83.9 d	0.889		0.004	0.2		0.0001	0.0003	0.002	
Ti*	^{51}Ti	5.79 m	0.320		10	7	70	700			

TABLE 2.6 (continued)

	Radio-nuclide	$t_{½}$	Photopeak energy	Possible interference	Calculated Detection Limits INAA (µg/g)	Calculated Detection Limits β-counting (µg)	Experimental Detection Limits Retort Water Fox et al.(1978) (µg/ml)	Experimental Detection Limits Shale Oil Kovar (1979) (µg/g)	Experimental Detection Limits Sea Water Kovar (1979) (µg/g)	Experimental Detection Limits Limestone Kovar (1979) (µg/g)	Comments
V	^{52}V	3.75 m	1.434	^{52}Cr(n,p)^{52}V	0.1	0.04	0.9		220,000	20,000	
Cr*	^{51}Cr	27.8 d	0.320		0.2	-	0.2	0.2	0.08	3	
Mn	^{56}Mn	2.58 hr	0.847	^{56}Fe(n,p)^{56}Mn	0.005	0.0004	0.9	0.001	2	0.1	exact t_d **important**
Fe*	^{59}Fe	45.6 d	1.095		40	1,000	20	2	8	100	
Co	^{60m}Co	10.5 m	0.059		0.9	0.002					
	^{60}Co	5.26 y	1.173		0.07	4	0.09	0.03	0.02	0.4	
Ni*	^{65}Ni	2.56 hr	1.481		50	0.4	0.7	10	3	500	exact t_d **important**
	^{58}Co										
Cu	^{64}Cu	12.8 hr	0.511 (β^+)		0.2	0.02					
	^{66}Cu	5.10 m	1.039		9	0.2	90	0.2	800	6	
Zn	^{65}Zn	245 d	1.115		5	90	3	0.6	0.2	5	
	^{69m}Zn	13.8 hr	0.439		20	20					
Ga	^{70}Ga	21.1 m	1.040		90						
	^{72}Ga	14.1 hr	0.835	^{56}Mn (0.847)	0.4	0.02	20	0.2	35	6	
Ge	^{75}Ge	82.0 m	0.265		2	0.04	300	2	700	60	exact t_d **important**
As	^{76}As	26.4 hr	0.559		0.5	0.02		0.03	10	0.1	
Se*	^{75}Se	120.4 d	0.265		2	-		0.08		0.3	
	^{77m}Se	17.5 sec	1.61	Ta (0.172)	50	-					
Br	^{80}Br	17.6 m	0.618		0.5	0.005				0.04	
	^{82}Br	35.3 hr	0.554		1.0	0.09	0.01	D			
Rb*	^{86}Rb	18.7 a	1.078		7	4	1	0.7	0.5	9	
	^{88}Rb	17.8 m	1.863		100	0.9					
Sr	^{87}Sr	2.83 hr	0.388		0.9	0.09	20	5	500	40	
Y	^{89m}Y	16.1 sec	0.915		1,000	-	3,000	60	15,000	4,000	
	^{90}Y	64.0 hr	-		-	0.2					
Zr	^{97}Zr	17.0 hr	0.747	^{154}Eu (0.757)	200	20	2,000	100	90	700	
Nb	^{94m}Nb	6.29 m	0.871		100	0.09	100	100	60	600	

TABLE 2.6 (continued)

	Radio-nuclide	$t_{1/2}$	Photopeak energy	Possible interference	Calculated Detection Limits INAA (μg/g)	Calculated Detection Limits β-counting (μg)	Experimental Detection Limits Retort Water Fox et al.(1978) (μg/ml)	Experimental Detection Limits Shale Oil Kovar (1979) (μg/g)	Experimental Detection Limits Sea Water Kovar (1979) (μg/g)	Experimental Detection Limits Limestone Kovar (1979) (μg/g)	Comments
Mo	^{99}Mo	66.7 hr	0.181		100	2			1	6	
	^{101}Mo	14.6 m	0.191		30	2	4				
Ru	^{103}Ru	39.5 d	0.497		0.1	9	0.5	0.2	0.1		
	^{105}Ru	4.44 h	0.726		4	0.2					
Rh	^{104m}Rh	4.41 m	0.051		0.02	0.07	4	8		8	need LEPD, $t_{1/2}$ short
Pd	^{109m}Pd	4.69 m	0.188		9	10	10	0.2			
	^{109}Pd	13.5 m	0.307		200	0.02			85	1	
Ag	^{108}Ag	2.42 m	0.632		2	0.09	0.3	0.2	0.08	1	
	^{110}Ag	24.2 sec	0.658		0.1	-					
Cd	^{111m}Cd	48.6 m	0.247		20	10					
	^{115}Cd	53.5 hr	0.53		0.4	0.09	3	0.8	5	7	
In	^{116m}In	54.0 m	1.293		0.01	0.0005	0.1	0.001	0.4	0.7	
Sn	^{125m}Sn	9.5 m	0.325		20	5	5	6	8	200	
Sb	^{122m}Sb	4.2 m	0.0607		10	-					
	^{122}Sb	2.8 d	0.564		0.02	0.09		0.03	0.02	0.01	
Te	^{131}Te	24.8 m	0.150		9	0.5	2				
	^{131}I	8.05 d	0.364		2	40		0.5	0.2	5	
I	^{128}I	25.0 m	0.411		1	0.02	8	0.002	70	40	
Cs	^{134m}Co	2.90 hr	0.128		0.4	0.04			0.009		
	^{134}Co	2.05 y	0.605		0.04	5	0.05	0.03		0.2	
Ba	^{139}Ba	82.9 m	0.166		10	0.5	4	0.4	2	200	
La	^{140}La	40.2 hr	1.596		1	0.04	0.3	0.04	0.7	0.8	
Ce	^{141}Ce	32.5 d	0.145		0.2	20	0.2	0.2	0.1	4	
	^{143}Ce	33.0 hr	0.293	^{59}Fe(0.143)	40	2					
Pr	^{142}Pr	19.2 hr	1.57		9	0.01	170	2	100	20	
Nd	^{147}Nd	11.1 d	0.091		0.2	2	0.3	0.2	0.2	4	

TABLE 2.6 (continued)

	Radio-nuclide	$t_{1/2}$	Photopeak energy	Possible interference	Calculated Detection Limits INAA (μg/g)	Calculated Detection Limits β-counting (μg)	Experimental Detection Limits Retort Water Fox et al.(1978) (μg/ml)	Experimental Detection Limits Shale Oil Kovar (1979) (μg/g)	Experimental Detection Limits Sea Water Kovar (1979) (μg/g)	Experimental Detection Limits Limestone Kovar (1979) (μg/g)	Comments
Sm	^{153}Sm	46.8 hr	0.103		0.2	0.009	0.1	0.004	0.01	1	
Eu	^{152m}Eu	9.3 hr	0.963	Fe (1.095)	0.09	0.00009	0.05		0.2		
	^{152}Eu	12.7 y	0.122		0.0007	-		0.00009		0.0009	
Gd	^{159}Gd	18.0 hr	0.363		9	0.1		5	80	8	
Tb	^{160}Tb	72.1 d	0.966		0.02	0.5	0.007	0.004	0.005	0.09	
Dy	^{165}Dy	139 m	0.095		0.0002	0.04	0.2	0.008	0.7	1	need LEPD
Ho	^{166}Ho	26.9 hr	0.0806		0.04	0.004	0.06	0.02	0.1	0.3	
Er	^{171}Er	752 hr	0.308		0.4	0.05		0.3	60	2	
Tm	^{170}Tm	134 d	0.084		0.04	0.2	0.01	0.01	0.02		
Yb	^{175}Yb	101 hr	0.396		0.02	0.04	0.03	0.005	0.01	0.5	
Lu	^{176m}Lu	3.69hr	0.088		0.009	0.0009	0.006	0.002	0.001	0.05	
Hf	^{179m}Hf	18.6 sec	0.217		7	-					
	^{181}Hf	42.5 d	0.482		0.03	2	0.07	0.008	0.009	0.2	
Ta	^{182m}Ta	16.5 m	0.172		40	2					
	^{182}Ta	115.1 a	1.122		0.05	0.9	0.01		0.01	0.06	
W	^{187}W	23.9 hr	0.479		0.7	0.02	0.6	0.04	0.7		
Re	^{186}Re	88.9 hr	0.137		0.04	0.02	0.02		0.009	0.02	
	^{188m}Re	18.7 m	0.106		4	0.07					
	^{188}Re	16.7 hr	0.155		0.2	0.004		0.02			
Os	^{190m}Os	9.9 m	0.361		400	-					
	^{191}Os	15.0 d	0.129		0.04	2	0.02	0.02	0.02	0.2	
	^{193}Os	31.5 hr	0.139		50	0.4					
Ir	^{192m}Ir	1.42 m	0.058		7	-					
	^{192}Ir	74.2 d	0.317		0.00004	0.05	0.0004	0.0003	0.0001	0.002	
	^{194}Ir	17.4 hr	0.328		0.1	0.002					
Pt	^{199}Pt	31.0 m	0.197		20	0.4					
	^{199}Au	3.15 d	0.158		0.1	2	0.5	0.1	0.9	40	

TABLE 2.6 (continued)

					Calculated Detection Limits		Experimental Detection Limits				
	Radio-nuclide	$t_{1/2}$	Photopeak energy	Possible interference	INAA (µg/g)	β-counting (µg)	Retort Water Fox et al.(1978) (µg/ml)	Shale Oil Kovar (1979) (µg/g)	Sea Water Kovar (1979) (µg/g)	Limestone Kovar (1979) (µg/g)	Comments
Au	^{198}Au	2.70 d	0.412		0.0005	0.005	0.005	0.001	0.002	0.003	
Hg	^{197}Hg	65.0 hr	0.0776		0.02	-	0.1	0.04	0.02	0.1	
	^{199m}Hg	43.0 m	0.158		100	-					
Tl*	^{204}Tl	3.81 y	-		-	50	450				uses different reacting
	^{206}Tl	4.19 m	-		-	4					
Pb*	^{209}Pb	3.30 hr	-		-	200					
	^{207m}Pb	0.80 sec					18,000	2,000	870,000	310,000	
Bi	^{210}Bi	5.01 d	-		-	5					
Po											
At											
Fr											
Ra											
Ac											
Th	^{233}Pa	27.0 d	0.313		0.01	0.7	0.02	0.008	0.006	0.2	
Pa											
U	^{239}Np	2.35 d	0.106		0.004	0.07	1	0.01	0.04	0.2	
sample size (g)					1,10	1,10	1.2,34	7-30	0.5-20	0.5-20	
neutron flux ($cm^{-2}sec^{-1}$)					10^{12}	10^{12}	$1.8\text{-}2.5\text{x}10^{12}$	$2.5\text{x}10^{12}$	$2.5\text{x}10^{12}$	$2.5\text{x}10^{12}$	
irradiation times (minutes)					60	60	1,30	30	30	30	
decay times					0	0	1 min 1 hr 1,7,20 d	1 hr 1,7,21 d	1 hr 1,7,21 d	1 hr 1,7,21 d	

D: element was detected

*: detectability is sometimes enhanced by the presence of epithermal and fast neutrons in the reactor

t_d: decay time

-: indicates the absence of β5 or γ radiation

It should be clear by now that detection limits may vary orders of magnitude depending on the exact procedure, equipment, and sample type. Nevertheless, variations of this nature are usually predictable. For example, for long lived isotopes where counting rates are not limiting, increasing the sample size by a factor of ten often improves detectability correspondingly. It is thus helpful to determine detection limits for a postulated analytical scheme, and then to extrapolate these to other types of samples.

Columns 6-11 in Table 2.6 therefore present experimentally determined detection limits (DL's) for different sample types. Columns 6-7 present detection limits which have been calculated by postulating the analytical conditions listed in Table 2.7, which reasonably reflect common laboratory operation. The activity of each isotope was calculated according to equation 2.1, and isotope activities were converted into counting rates by considering the efficiency of the detector. For the most part these data follow Guinn (1971), but with somewhat more conservative assumptions reflecting the complexity of most "real world" samples. Additional nuclear data is from Lederer et al. (1967), and detector efficiency curves from Dams (1976).

Several general observations can be made based on the first six columns of Table 2.6. First, the elements H-O are completely inappropriate for thermal neutron activation either because no γ-active species is produced or because detection limits are greater than 100% of the sample weight. The elements Po-U are naturally radioactive so that their detection is usually by direct γ spectroscopy, although Th and U can also be measured with reasonable detectability using INAA. Several other isotopes ^{32}P, ^{90}Y, ^{204}Tl, ^{209}Pb, ^{210}Bi produce no γ radiation and can therefore be detected only by β counting. It is also noteworthy that detectabilities are generally better for β counting than for INAA, although the latter is seldom used because of higher costs and the requirement for complex sample manipulation.

TABLE 2.7. CONDITIONS WHICH HAVE BEEN ASSUMED FOR THE CALCULATED DETECTION LIMITS SHOWN IN TABLE 2.6

neutron flux, ϕ	10^{12} cm^{-2} sec^{-1}
irradiation time, t_e	1.0 hr
decay time, t_d	0.0
γ detector	Ge(Li), 50 cm^3
efficiency of γ detector	10% with respect to a 3" x 3" NaI(Tl) detector at 2 cm distance
minimum detectable β count rate	1000 min^{-1} for $t_{1/2} < 1$ hr 100 min^{-1} for $t_{1/2} > 1$ hr

Minimum detectable γ count rate for full-energy peak:

$t_{1/2}$	count rate	sample size	counting time	total full energy counts
$t_{1/2} < 1$ min	10,000 min^{-1}	1.0 g	1.0 min	10^4
1 min $< T_{1/2} <$ 1 hr	1,000 min^{-1}	1.0 g	10 min	10^4
1 hr $< t_{1/2} <$ 2 d	100 min^{-1}	1.0 g	100 min	10^4
2d $< t_{1/2} <$ 14d	10 min^{-1}	10.0 g	100 min	10^3
14d $< t_{1/2}$	1 min^{-1}	10.0 g	1000 min	10^3

Columns 8-11 contain detection limits reported by Fox et al. (1979) and Kovar (1979) for samples similar to those expected from an oil shale industry. Analytical conditions which are shown at the bottom of the table, are generally similar to those postulated for column 6 except for a larger sample of shale oil and the absence of the short (one minute) exposure and decay time for the shale oil, sea water, and limestone.

It is noteworthy that the calculated detection limits are normally within a factor a ten of the empirical detection limits, and that the exceptions can be predicted for several reasons: the empirical detection limits for shale oil are normally lower than those in column 6, as would be expected for the larger sample of shale oil used in the analysis; the shale oil, sea water, and limestone samples, which underwent no one-minute exposure and decay period, exhibit greatly degraded detection limits for elements with half lives on the order of a few minutes, such as Mg, Al, Ti, Rh and S; and the spectra of sea water is entirely dominated by the 1.37 and 2.75 MeV Na lines, so that in essence no other element can be detected until the ^{24}Na has decayed. Thus, sea water elements with half lives much longer than 15 hours exhibit DL's similar to those in column 6, while elements with half lives comparable to or shorter than 15 hours exhibit much poorer DL's.

The last column in Table 2.6, in conjunction with the column showing potential interferences, also helps explain variations seen in columns 6-11. Elements such as Rh and Dy, which are both short lived and emit γ radiation below the 0.100 MeV level, need a LEPD or Si(Li) detector for best detectability. However, samples were actually measured using normal Ge(Li) detectors. For selected elements the decay time, t_d, may be important for two reasons: first, for elements such as Mn, Ni, Ge, and Si with $t_{\frac{1}{2}}$ of a few hours, the exact decay time significantly influences the detected count rate, although not all samples can be counted at precisely 1.0 hours. Second, as an artifact in calculating the detection limits in column 6, detectability improves 100 times as $t_{\frac{1}{2}}$ increases from 1.99 to over 2.00 days, although DL's in fact change more continuously with $t_{\frac{1}{2}}$. In the interest of continuity, elements with $t_{\frac{1}{2}}$ slightly over two days (Cd) could therefore be increased ten fold, while elements with $t_{\frac{1}{2}}$ slightly less than 2 days (La, Sm) could be decreased ten fold, thereby bringing these calculated DL's more in agreement with empirical measurements.

The approach to detection limits described in this section is, of course, over-simplified. A more realistic approach would be to calculate the entire expected spectrum including Compton background and interfering lines. The DL could then be calculated based on background noise and interferences. However, at the present I am unaware of an algorithm designed for this purpose, and suggest the approach described above.

Although this section has treated only neutron activation carried out with a reactor neutron source, activation analysis with 14-MeV neutrons from neutron generator should not be entirely neglected. The reader is referred to Quinn (1971), Perdyn (1967), and Fujii et al. (1969) for tables of detection limits for 14-MeV neutron activation.

In general, detectabilities for most elements are better by several orders of magnitude with thermal NAA than with fast neutron activation. The exceptions include N, O, and possibly Se, Fe, F, Cr, Ni, Rb, and Se. Also, interference problems become worse with fast neutrons because of the additional number of possible reactions, such as (n,p), (n,n'), (n,2n') and (n,2) processes. Nevertheless, fast neutrons are routinely used for O and have been suggested for N, A, Fe, Mg, and Si. The reader is referred to Cornelius et al. (1976) for applications of fast neutron activation.

Accuracy and Precision

For those elements which are present at levels several times their detection limit under interference free situations, INAA is usually considered a reference method for several valid reasons. First, because of the penetrating nature of neutrons and γ-radiation, matrix effects are minimal. The exceptions are samples of high neutron cross section (e.g. Cd, B), or elements which emit soft γ-rays in a highly X-ray absorbing material (e.g. Rh in Pb). Second, although several potential interferences have been noted in this text, their occurrence is less than in most multi-element techniques and, perhaps more importantly, interferences can be predicted and recognized. Third, INAA is usually performed with no sample digestion or pretreatment, thereby minimizing the potential for sample loss or contamination.

The accuracy and precision of INAA for environmental samples have been discussed by several authors. Ondov et al. (1975) report on a 4-laboratory intercomparison of the analysis of coal and fly ash by INAA. Intralaboratory precision was approximately ± 10% (one standard deviation), for the coal sample; interlaboratory precision (and by implication, accuracy) was $\leq$ 15% for 26 of the 30 elements. Fox et al. (1979) report an interlaboratory variation of approximately ±20% in retort water. These variations are probably typical of complex samples. On the other hand, for the identification of pottery fragments, where more precise analyses are required, Perlman et al. (1978) report an interlaboratory precision of 0.3% (one sigma) under ideal conditions. Perlman et al. (1978) also compare the results of pottery analyses from two laboratories and report an interlaboratory agreement of 1%, although this figure should not be considered typical of routine work.

2.2.2 Other Activation Procedures

As mentioned earlier, many other nuclear activation techniques have been reported in addition to neutron activation. A selection of such methods is shown in Table 2.8, along with the detected elements. Here prompt γ spectroscopy implies that the emitted γ radiation was detected during, as opposed to after, the irradiation. One of the most promising of these techniques is prompt γ-ray activation analysis spectrometry as described by Faily et al. (1979). This approach often complements INAA by detecting most readily those elements which are least sensitive by INAA (e.g. B, N, Gd, and F), while at the same time using many of the same instruments.

The scope of this text does not permit extensive discussions of each of the techniques shown in Table 2.8, and the reader is referred to the literature found in the table for additional information.

TABLE 2.8. LESS COMMON ELEMENTS WHICH HAVE BEEN MEASURED BY ACTIVATION METHODS

Elements	Description	Reference
U, Th	Delayed neutron emission from USGS standard rocks	Millard (1976)
Bi	α spectroscopy of ^{210}Po produced by the reaction $^{209}Bi\ (n,\gamma)\ ^{210}Bi \rightarrow \beta^{-} + ^{210}Po$ in USGS standard rocks	Greeland et al. (1976)
'H	Prompt γ spectroscopy of the $'H(n,\gamma)^{2}H$ reaction	Bowen (1975)
B, N, Si, C, O	Charged particle activation	Bowen (1975)
C, N, O	Instrumental Photon Activation Analysis	Bowen (1975)
Sm, Gd	Prompt γ activation analysis with neutron excitation	Lombard and Isenhour (1969)
O	^{3}He activation of Be, Th, and Mylar samples	Markowitz and Mahoney (1962)
B, U	Detected particle tracks from $B(n,\alpha)$ and $U(n,f)$ reactions	Fleischer and Lovett (1968)
N	N in hydrocarbons by n activation with an n generator	Fujii (1969)

TABLE 2.8 (continued)

Elements	Description	Reference
B	Prompt γ spectrometry from ^{10}B (n,α) ^{7}Li reaction	Cornelius et al. (1976)
B, N, C, O	Charged particle activation	Cornelius et al. (1976)
Si, O, F, P	n Activation with neutron generator	Cornelius et al. (1976)
N, O, Si, F, Se, Tl, Pb, P	Activation with fast neutrons	Guinn (1969)
Gd, H, C, Li, B, Cd	Prompt γ spectrometry with n excitation	Guinn (1969)
F, Pt, Sc, Se, W, Pb, Li, B	n activation with pulsed reactors	Guinn (1969)
C, N, O, F	Photon activation analysis	Guinn (1971)
B, Cd	Prompt γ-ray spectrometry with thermal n excitation	Gladney et al. (1976)

TABLE 2.8 (continued)

Elements	Description	Reference
S, Ce, K, Ca	^{3}He activation - γ-ray spectrometry	Lee and Murkowitz (1974)
F	^{3}He activation - γ-ray spectrometry	Lee et al. (1971)
C, N, S	Prompt γ-ray spectrometry with p+ activation	Macias et al. (1978)
H, B, C, N, Na, F, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Cu, Zn, As, Se, Br, Mo, Cd, In, Nd, Sm, Gd, Pb	Prompt γ-ray activation analysis with thermal n excitation	Faily et al. (1979)

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2.3 X-Ray Fluorescence

This section covers both wavelength dispersive (WD) and energy dispersive (ED) X-ray fluorescence spectroscopy (XRF). Particle induced X-ray emission (PIXE) is also treated. This discussion assumes the reader is already familiar with the basic instrumentation and XRF spectrum. The reader needing more detailed information is referred especially to the text by Herglotz and Birks (1978) for a concise and readable introduction, as well as to the other citations in Table 2.9.

The detection limits achievable by XRF have been discussed extensively in the literature from both theoretical and practical perspectives. (See Table 2.9 for an introduction to the literature on this subject). The main factors determining the detectability of both ED and WD X-ray spectrometer are summarized in Table 2.10. Except at absorption edges the properties shown in Table 2.10 vary smoothly in going from one element to the next in the periodic table. For this reason detection limits also vary continuously, and knowing the detection limits for a few elements enables the analyst to extrapolate to others (Giauque, 1972; Rhodes, 1973).

The instrumental factors shown in the table vary between laboratories and should be ascertained by type prior to submitting a sample for analysis. One such variation is the power level of the X-ray source. In WD/XRF the signal-to-background ratio improves in direct proportion to the power level of the X-ray tube; detectability therefore improves as the square root of the power level of the source. For both ED and WD spectrometry, elements are most efficiently excited by radiation slightly more energetic than their fluorescent radiation. Selecting the proper excitation source can therefore determine whether a particular element is detected. The nature of the sample can also greatly affect the success of the analysis. For example, in ED spectrometry the detector is easily saturated by radiation scattered from the detector, making essentially every element undetectable. This situation is most likely to occur with

TABLE 2.9. RECENT LITERATURE ON X-RAY FLUORESCENCE SPECTROSCOPY

Principles and Instrumentation

Radioisotope excited ED/XRF	Rhodes (1971)
Automated optimization of ED/XRF for multi-element analysis	Kneip & Laurer (1972) Wegscheider et al. (1978)
Determination of the oxidation states S compounds in mixture	Birks & Gilfrich (1978)
Instrumental interferences in ED/XRF	Bonner (1979)
Proton induced X-ray emission	Vis & Verheul (1975)
The use of polarized X-rays to minimize background	Ryon (1977) Ryon & Zahrt (1979)
A compact WD analyzer for S in particulate matter	Birks et al. (1977)
Detection of C, N, O, and F	Russ et al. (1976)
Characteristics and electronics of the Si(Li) detector	Gedcke (1972) Jaklevic & Goulding (1970)
A comparison of WD and ED spectrometers	Porter & Woldseth (1973)
ED instrument characteristics	Frankel & Aitken (1970)
Comprehensive review	Herglotz & Birks (1978)

Detection Limits

With various radioisotope sources	Rhodes (1973)
For biological materials and air filter samples	Giauque et al. (1973)
A comparison of seven commercial instruments for water analyses	Birks and Gilfrich (1978)
Theoretical calculations	Pantony & Hurley (1972)
Parameters affecting air filter analyses theoretical calculations	Birks (1977)
A comparison of wavelength and energy dispersion, with various excitation sources	Gilfrich et al. (1973) Birks et al. (1972)

TABLE 2.9 (continued)

Detection Limits	
For coal, coke, and fly ash, using tube excitation and energy dispersive detectors	Cooper et al. (1976)
A comparison of PIXE and XRF	Sheer et al. (1977) Birks (1972)
Methodology	
S in fuel oil by ED/XRF	Trovato et al. (1979)
Interlaboratory comparison with air filter samples	Camp et al. (1974)
Preconcentration of trace elements in water samples by precipitation with polyvinylpyrrolidone & thionalide	Panayappan et al. (1978)
Analysis of airborne dust and fumes	Cares (1968) Luke et al. (1972) Jakelvic et al. (1973) Rhodes et al. (1972) Bodart et al. (1973)
Preparation of thin samples from geological materials, standardization, background correction, self-absorption effects, and spectral interferences	Giauque et al. (1977)
Silica gel standards	Breitwieser & Lieser (1978)
Corrections for self absorption and spectral background in light matrices	Giauque et al. (1979)
Calibration with thin-film standards corrections for interelement effects	Giauque et al. (1976)
Co-precipitation techniques for concentrating trace metals in water	Kessler et al. (1979)
Concentration of trace elements in water into thin films	Disam et al. (1979)
Geochemical materials, using ED/XRF with tube excitation	Giauque et al. (1977)
Airborne particulate matter, using radioisotope sources	Rhodes et al. (1972)

TABLE 2.9 (continued)

Methodology	
Airborne particulate matter, using X-ray transmission tubes and secondary fluorescers	Giauque et al. (1975) Jaklevic et al. (1973) Hammerle et al. (1973)
Oil shale, shale oil, and retort water	Dickman et al. (1977) Fruchter et al. (1979) Fox et al. (1978)

TABLE 2.10. PHYSICAL AND INSTRUMENTAL PARAMETERS WHICH DETERMINE THE DETECTABILITY OF X-RAY FLUORESCENCE

Physical Properties

Absorption cross section
Fluorescent yield
Excitation intensity and energy distribution
Raleigh and Compton scattering cross section

Instrumental Variables Wavelength Dispersive	Instrumental Variables Energy Dispersive
X-ray tube composition and power level	Type of excitation source transmission tube
Vacuum, He, as air path	secondary fluorescer
Monochromator efficiency	radioisotope particles
Detector efficiency and solid angle	Detector efficiency and sample detector geometry
Number of X-ray sources used for each sample	Number of X-ray sources used for each sample
Exposure time	Extent to which Raleigh and Compton peaks are degraded to background continuum
	Exposure time

thick, low atomic weight samples. For either WD or ED spectrometry, detectability also improves with exposure time.

Both WD and ED spectrometry respond to the concentration of element per unit area, and detection limits are normally stated in these terms. For single elements deposited on Whatman cellulose filter paper, Gilfrich et al. (1973) experimentally determined such limits for both WD and ED spectrometers and reported on the effects of spectrometer resolution, source intensity, and excitation media (X-ray tubes, radioisotopes, and particles).

Table 2.11 summarizes the detection limits of Gilfrich et al. for optimum yet realistic conditions. It must be emphasized that these limits are for interference-free samples and as such represent the "best achievable." Nevertheless, they are also frequently achieved in practice, as evidenced by several reports cited in Table 2.9. Figure 2.1 illustrates the continuous variation of detectability with atomic number.

The areal concentration limits in Table 2.11 and Figure 2.1 can be converted to mass concentration limits by assuming a sample density. For example, an air filter sample could contain a deposit of approximately 100 $\mu g/cm^2$. The detection limit for Cu using a WD spectrometer with a Cr X-ray tube would then be 1000 µg/g, or for an aerosol containing 100 $\mu g/m^3$ total particulate matter, 100 ng/m^3.

In theory, detection limits should improve with increasing sample thickness. In reality, self-absorption effects become increasingly severe with thick samples. The maximum permissible sample thickness depends on the energy of the characteristic X-rays and hence the atomic number of the element; however, sample density is normally kept below 1-10 mg/cm^2 (Rhodes, 1973; Gilfrich 1973) unless adequate self absorption corrections are applied to the data. Under these circumstances the detection limits for bulk samples are typically in the range of 1 to 100 µg/g, as is illustrated in Figures 2.2 and 2.3. As can be seen, using

TABLE 2.11. DETECTION LIMITS FOR VARIOUS X-RAY TECHNIQUES (ng/cm^2). Exposure time is 100 sec unless noted otherwise. Limits were measured experimentally from single element standards on cellulose filter paper except for proton excitation, for which nitrocellulose filters were used (Gilfrich et al., 1973).

	Wavelength Dispersion[a]			Energy Dispersion									
				Radioisotope[b] Excitation		Secondary Fluorescer[c] Excitation				X-ray Tube[d] Excitation			Proton Excitation[f]
	Cr tube	Rh tube	W tube	^{55}Fe	^{109}Cd	Mn	Cu	Ag	Cr/Zr	Mo	W	W[e]	
Al	200	50	-	-	-	-	-	-	-	-	-	-	-
S	30	8	30	-	-	-	-	-	-	-	-	600	-
K	2	10	-	-	-	-	-	-	-	-	-	200	0.2
Ca	6	20	-	80	3000	30	30	200	40	400	30	100	-
V	30	20	20	100	1000	20	30	200	-	200	30	90	-
Fe	90	20	22	-	1000	-	20	-	200	100	40	100	-
Cu	100	30	20	-	-	-	-	-	-	-	-	-	0.5
Zn	100	30	-	-	700	-	-	80	100	100	200	100	-
Se	500	90	60	-	200	-	-	30	20	50	100	80	-
Br	200	100	100	-	-	-	-	-	-	-	-	-	0.2
Zr	-	-	-	-	100	-	-	20	-	-	-	-	-
An	-	-	-	-	-	-	-	-	-	-	-	-	1
Pb	600	200	-	-	400	-	-	80	-	100	200	100	-

[a] 2500 watts x-ray tube, vacuum spectrometer
[b] 150 mCi
[c] Excited with 2500 watt W X-ray tube
[d] Power sufficient to maintain a detector count rate of 10,000 sec^{-1}
[e] W tube with Ni filter
[f] 50 μC exposure, 5 MeV proton energy

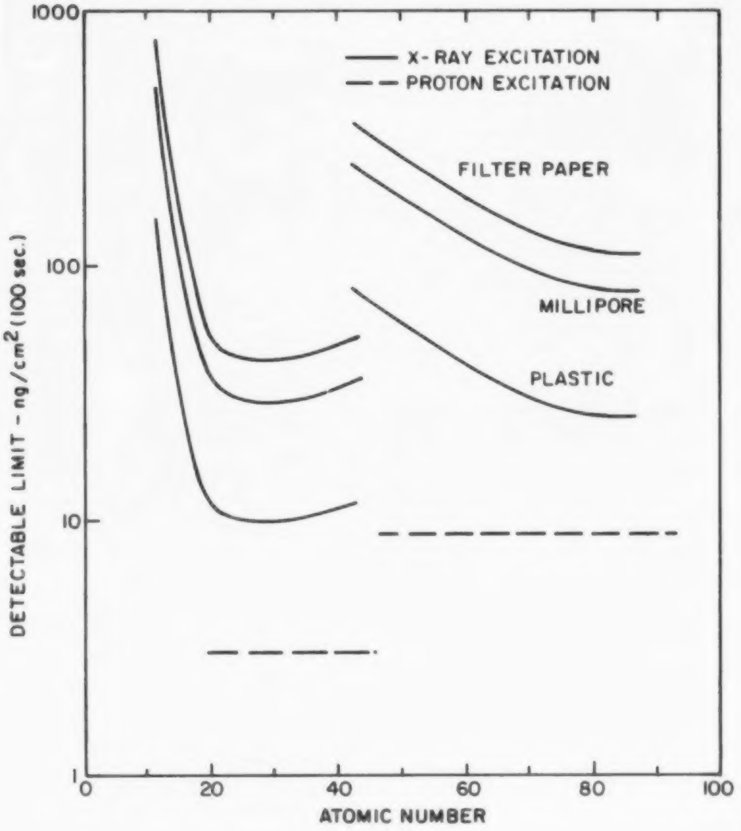

FIGURE 2.1. LIMITS OF DETECTIBILITY AS A FUNCTION OF ATOMIC NUMBER. THE BREAK AT $Z \approx 45$ IS WHERE ONE CHANGES FROM K TO L SPECTRA. REPRINTED WITH PERMISSION FROM BIRKS (1972).

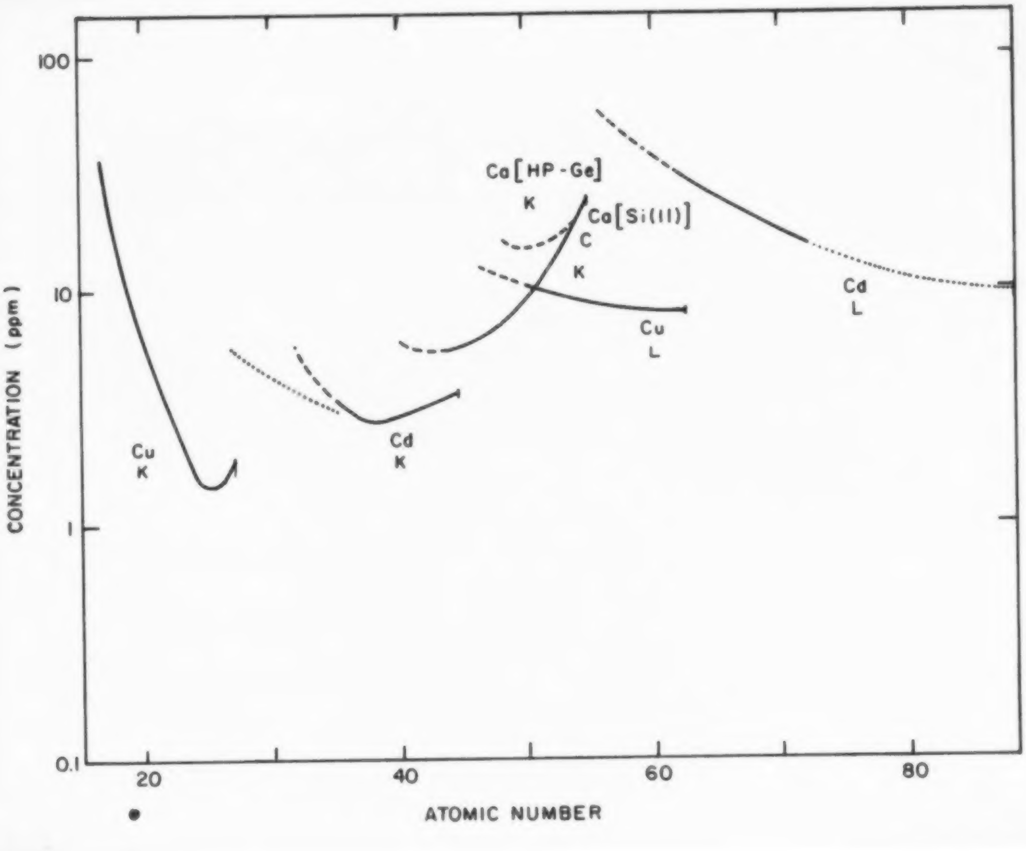

FIGURE 2.2. LIMITS OF DETECTABLE MASS CONTENT FOR THE XRF SYSTEM UNDER STANDARD RUNNING CONDITIONS USING Cu, Cd, Ce AS SECONDARY FLUORESCERS. THE DOTTED CURVES INDICATE EASILY ACHIEVABLE DETECTION LIMITS WHEN USING SANDWICH SHIELDING INSTEAD OF TANTALUM. FROM SHEER et al (1977).

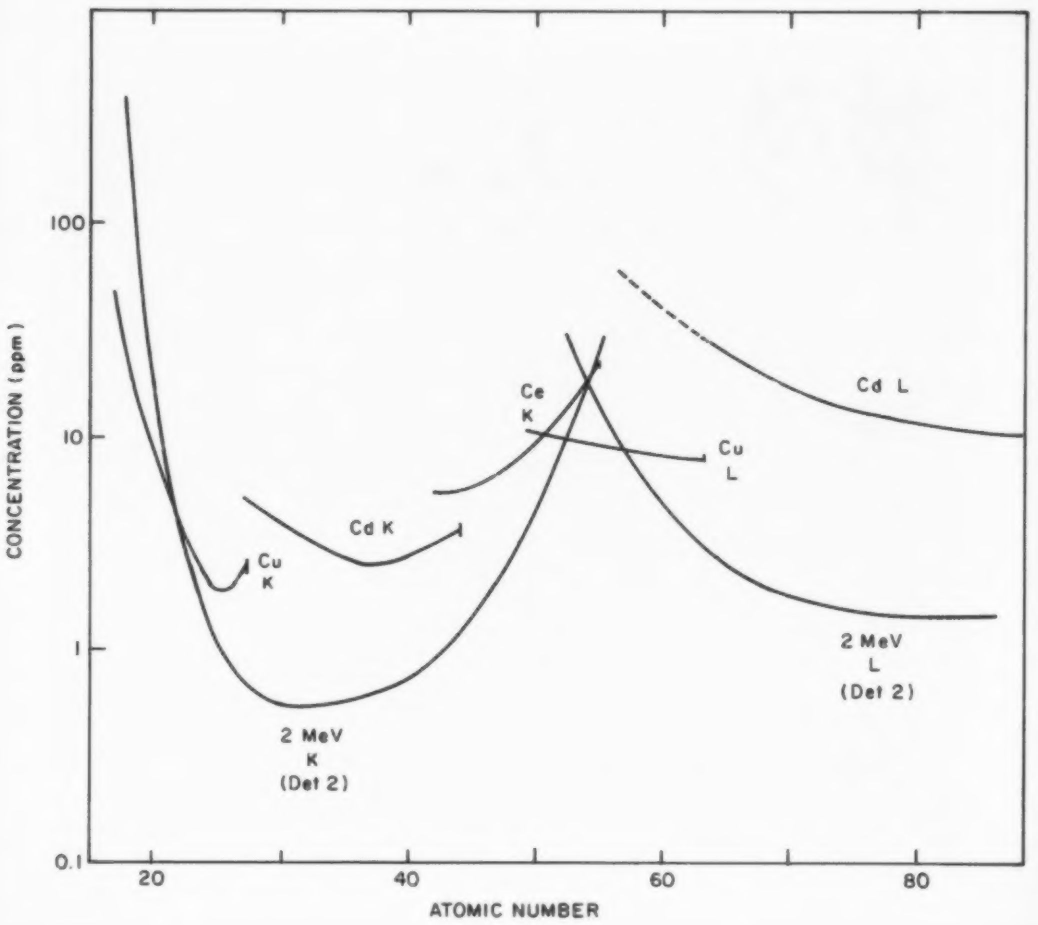

FIGURE 2.3. SENSITIVITY OF PIXE AND XRF SYSTEMS FOR BIOMEDICAL SAMPLES CONTAINING 3% KCl (PIXE: 2 MeV; 1500s; 100μC; 0.085 sr; 50μm Al ABSORBER--XRF; Cu, Cd, Ce, 3x1000s; 0.010sr; 25μm KAPTON ABSORBER). FROM SHEER et al (1977).

X-ray excited X-ray fluorescence, several secondary fluorescence sources were required in order to achieve uniform detectability, while proton induced X-ray emission provided more uniform coverage with a single exposure. By applying corrections for self-absorption, geological samples on the order of 1 g/cm^2 have been analyzed successfully for elements heavier than Sc by Giauque et al. (1977). They reported detection limits in the range of 1-10 μg/g for several elements.

The detection limits discussed in the previous paragraphs should be considered the "best achievable" for simple systems. In the routine analysis of complex environmental samples, not every element which is above the detection limits discussed in the preceeding pages will necessarily be detected due to the following practical and instrumental problems: Multichannel, wavelength dispersive spectrometers are limited to the number of monochromators on the instrument and only preselected elements will be detected. Scanning, wavelength dispersive spectrometers can theoretically detect every fluorescing element in the periodic table, but with considerably poorer detectability than the multichannel instruments. Absorption of the fluorescent X-rays by air in the monochromator is especially important for wavelength dispersive instruments because of their long optical pathlength. For this reason, elements below Ti are often not detected unless vacuum or He-filled monochromators are available.

The range of elements detected by ED/XRF is limited for different reasons. Elements lighter than Mg are not detected because their low-energy X-rays do not penetrate the detector window. Elements of atomic number slightly lower than that of the exciting radiation are lost in the Compton and Raleigh peaks. Elements below the Compton edge of the scattered radiation are also subject to increased background. In ED/XRF the finite counting rate of the semiconductor is also limiting: because all incident radiation must be processed, the more intense peaks occupy the detector and electronics to the exclusion of the less intense peaks. Intense peaks of this nature can arise either from X-ray scattering by low-Z samples or from X-ray fluorescence by other components in the sample. As a result of the finite counting rate, it is common that only the most highly fluorescent elements are detected during a single exposure. The best elemental coverage with ED/XRS is therefore obtained by using multiple exposures with a variety of X-ray sources, each of which is designed to most effectively excite different parts of the periodic table (Giauque et al., 1975; Rhodes et al., 1972).

Resolution problems can also limit the elemental coverage of ED/XRS. Most Si(Li) detectors are unable to resolve the K_α and K_β radiation of elements differing by one atomic number for elements lighter than Mn (depending to a degree on the exact detector design). Although such interferences can be compensated for mathematically, to a degree they nevertheless degrade detectability (Herglotz and Birks, 1978). This means, for example, that Sc should be less readily detected in limestone than in silica.

The method by which the sample is prepared into a form compatible with the X-ray spectrometer varies between laboratories and can also affect the accuracy of the analysis as well as the number of elements which can be successfully determined. Ideal samples are optically thin to both excitation and fluorescence radiation in order to avoid interelement effects.

To a first approximation, air filter samples satisfy this criterion and are therefore analyzed without additional preparation. This approximation assumes that the particles are deposited as a thin layer on the top of the filter so that no X-rays are absorbed by the filter material. This assumption may be adequate for heavier elements on thin membrane filters, but is questionable for the lighter elements (Mg-Cl), especially on fibrous glass filters.

Solid samples must be ground and homogenized or dissolved in molten salt in order to minimize mineralogical effects, and then prepared into a rigid form prior to introduction into the spectrometer. For example, Giauque (1977) ground a series of geological samples to 10-50 μm particles and pressed the resulting powder at 8000 psi into a lucite holder. The pellet was analyzed for 28 elements in the atomic weight range Ti to Ba. In Giauque's study the results of the XRF analyses agreed well with neutron activation analyses. Fruchter et al. (1979) employed this technique for the analysis of raw and spent oil shale and also achieved good agreement with neutron activation analyses. Integral to the pellet technique are rather extensive corrections for self-absorption and background shifts, so that significant software is required (Giauque al. 1977; Fruchter, 1979). In an earlier paper Giauque et al. (1973) also described a method for depositing geological specimens onto membrane filters, which were then analyzed as thin samples.

Liquid samples are either placed in X-ray transparent containers or are incorporated into thin, solid wafers. For example, Rhodes (1979) contained liquid samples between two thin sheets of Mylar. He reported that with this technique most elements could be detected in the range 5-50 μg/ml using radioisotope dilution. Fruchter et al. (1979) compared three different methods for analyzing retort waters. The first method consisted of evaporating ∿100 μl of sample onto a 1 cm diameter area and placing the sample in a constant-flux area of the spectrometer. This method was rapid, although self-absorption by organics could become a problem for low Z elements. The second method consisted of freezing a thin section of sample which was then exposed directly in the spectrometer. This approach resulted in relatively high scattering but minimized sample loss by evaporation. The third technique consisted of drying the sample onto cellulose powder and pressing the residue into a wafer. While Fruchter's group preferred the third method, the results from all three methods agreed well.

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2.4 Inductively Coupled Plasma Atomic Emission Spectroscopy

The revival of atomic emission spectroscopy as an analytical method for the routine analysis of waters and other liquids derives largely from the recent development of the inductively coupled plasma as an emission source. This development is chronicled by Fassel as well as other investigators, and the reader is referred to their original works for detailed information (Table 2.12). Here I attempt only to summarize those characteristics which distinguish inductively coupled plasma from the other analytical techniques discussed in this chapter.

Analysis by inductively coupled plasma-atomic emission spectroscopy (here referred to as ICP spectroscopy) requires that the sample be introduced as an aerosol into the argon plasma, where it is vaporized, atomized, and excited to optical emission.

As in other atomic emission techniques, radiation intensity at the characteristic wavelengths is measured after correction for spectral background. Up to 50 elements can be determined simultaneously using a polychromator with fixed slits, or the spectrum can be measured sequentially with a scanning monochromator. Because liquid samples are more readily formed into an aerosol than are solids, ICP spectroscopy is applied most commonly to the analysis of waters, oils, and organic solvents. Thus, ICP spectroscopy is a multielemental technique best suited for the analysis of liquids.

Several features distinguish the inductively coupled plasma from other optical emission sources. The plasma is maintained by inductive coupling to a radio frequency power supply. No electrodes are required, eliminating a source of contamination common to "arc and spark" sources. A major source of error in flame spectroscopy is the formation of refractory molecular species which results in the depression of atomic species. In ICP spectroscopy such interferences are eliminated or minimized due to the high plasma temperature (∿ 10,000 °K). Ionization interferences,

TABLE 2.12. INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY: AN INTRODUCTION TO THE LITERATURE

Basic principles and instrument design	Fassel (1979) Ward (1978) Fassel (1977) Boumans et al. (1976) Larsen & Fassel (1976) Boumans (1976) Larsen et al. (1975) Fassel (1974) Fassel & Kniseley (1974) Scott et al. (1974)
A Bibliography, 1959-1977	Bates et al. (1978)
Prominent emission lines	Winge et al. (1979)
ICP Newsletter	Barnes (1978)
Accuracy and interferences	Ward (1977)
Detection limits	Nikdel (1979) Meyer (1979) Workman (1979) Shelkoph (1979) Mermet (1977) Fassel (1974)
Hydride generation technique for As, Sb, Be, Se and Te in routine water quality testing	Garbarino & Taylor (1979)
Wear metals in lubricating oil	Fassel et al. (1976)
U in rocks	Scott et al. (1976)
Geochemical samples	Scott & Kokot (1975)
Botanical samples	Goodpasture et al. (1978)
Blood serum	Morrison (1977)
Metal alloys	Ward & Marciello (1979)

which result from the loss of neutral atoms in flame emission sources ionization processes, also appear minimal in the inductively coupled plasma.

Unlike some flame and arc sources, the inductively coupled plasma is an optically thin source and self-absorption is therefore minimized. This characteristic gives ICP spectroscopy a linear range of 10^4 to 10^5, permitting the simultaneous measurement of both major and minor elements. Finally, the inductively coupled plasma is sufficiently bright to produce detectable signals for elements at trace levels. Reproducibility of ICP spectroscopy is comparable to atomic absorption techniques (~ 10%).

A major disadvantage of ICP spectroscopy is the common occurrence of spectral interferences, both in the form of overlapping lines and changes in background intensity (Boumans, 1976). To an extent such interferences can be compensated for by measuring spectral background on every sample, or by measuring the concentration of interfering concomitants and applying mathematical correction routines. Nevertheless, corrective actions of this type are obviously limited, and such interferences may often force the analyst to select less sensitive analytical lines.

ICP spectrometers are normally purchased from commercial vendors as a complete package--including power supply, plasma torch, polychromator, and detector. Variations between the instruments can therefore be largely described by citing the manufacturer and model number. Once the spectrometer design is specified, the major factor determining detectability is the choice of analytical wavelength and the presence or absence of interfering elements in the sample.

Table 2.13 provides detection limits for ICP spectroscopy as determined by several workers using different instruments. The first five columns were determined using simple solutions containing only the analyte of interest and not the matrix elements which would be present in realistic samples. As such, they represent the best achievable detection

TABLE 2.13. DETECTION LIMITS FOR ICP SPECTROSCOPY

	Pure H_2O[b] standards	Pure H_2O[c] standards	Pure H_2O[d] standards	USGS Lab,[e] Mixed standards in 0.1 N HNO_3	Mixed standard[f] in H_2O	Hydride[g] generation	Commercial[h] laboratory	Mixed standard in[b] 10% HCl	Simulated soil[b] digest[a]	Lubricating oils[i] diluted 1:10 with MIBK
Li	0.3	--	--	4	--	--	--	--	--	--
Be	0.4	0.5	0.4	0.5	--	--	1	--	--	--
B	0.7	5	80	--	--	--	1000	2	30	--
Na	0.2	0.2	0.3	100-200	--	--	1000	10	--	--
Mg	0.01	0.7	0.05	4	--	--	8	0.4	--	7
Al	0.2	2	2	--	--	--	30	30	--	90
Si	10	10	--	4	--	--	6	--	--	70
P	20	40	70	--	--	--	200	30	--	--
S	--	--	--	--	--	--	--	--	--	--
K	--	--	--	--	--	--	100	100	--	--
Ca	0.02	0.07	0.02	20-100	--	--	30	2	--	0.4
Sc	--	3	--	--	--	--	--	--	--	--
Ti	0.07	3	0.2	--		--	1	2	--	30
V	0.2	6	0.2	6	--	--	1	--	--	30
Cr	0.3	1	0.3	--	--	--	7	3	10	30
Mn	0.06	0.7	0.06	1	--	--	1	1	--	10
Fe	0.3	5	0.3	3	--	--	4	3	--	40
Co	3	3	--	3	--	--	20	10	20	--
Ni	0.4	6	0.4	--	--	--	100	5	9	100
Cu	0.1	1	0.1	10	--	--	2	3	10	6
Zn	2	2	16	3	--	--	50	2	8	40
Ga	0.6	14	0.6	--	--	--	--	--	--	--
Ge	--	150	4	--	--	--	--	--	--	--
As	40	40	400	--	--	0.8	100	20	700	--
Se	--	30	--	--	--	1.0	--	20	200	--
Rb	--	--	--	--	--	--	--	--	--	--
Sr	0.02	0.02	--	0.5	--	--	1	0.6	7	--

TABLE 2.13 (continued)

	Pure H_2O[b] standards	Pure H_2O[c] standards	Pure H_2O[d] standards	USGS Lab,[e] Mixed standards in 0.1 N HNO_3	Mixed standard[f] in H_2O	Hydride[g] generation	Commercial[h] laboratory	Mixed standard in[b] 10% HCl	Simulated soil[b] digest[a]	Lubricating oils[i] diluted 1:10 with MIBK
Y	--	0.2	0.06	--	--	--	--	--	--	--
Zr	0.4	5	0.4	--	--	--	2	--	--	--
Nb	0.07	10	--	--	--	--	--	--	--	--
Mo	0.2	5	0.2	10	--	--	30	4	20	--
Ru	--	--	--	--	--		--	--	--	--
Rh	--	3	--	--	--	--	--	--	--	--
Pd	--	7	2	--	--	--	3	--	--	--
Ag	4	4	--	--	--	--	2	--	--	20
Cd	2	2	3	1	--	--	70	1	6	--
In	30	30	--	--	--	--	--	--	--	--
Sn	30	300	30	--	--	--	--	--	--	--
Sb	200	200	--	--	--	--	--	--	--	30
Te	--	80	--	--	--	1.0	--	--	--	--
Cs	--	--	--	--	--	--	--	--	--	--
Ba	0.02	0.1	0.02	2	--	--	30	1	1	--
La	0.05	3	0.4	--	5	--	--	--	--	--
Ce	0.7	7	2	--	20	--	--	--	--	--
Pr	--	--	--	--	20	--	--	--	--	--
Nd	--	50	--	--	10	--	--	--	--	--
Pm	--	--	--	--	--	--	--	--	--	--
Sm	--	20	--	--	20	--	--	--	--	--
Eu	--	1	--	--	3	--	--	--	--	--
Gd	--	7	--	--	10	--	--	--	--	--
Tb	--	200	--	--	9	--	--	--	--	--
Dy	--	4	--	--	8	--	--	--	--	--
Ho	--	10	--	--	8	--	--	--	--	--
Er	--	1	--	--	10	--	--	--	--	--
Tm	--	7	--	--	6	--	--	--	--	--
Yb	--	0.9	0.04	--	2	--	--	--	--	--

TABLE 2.13 (continued)

	Pure H_2O[b] standards	Pure H_2O[c] standards	Pure H_2O[d] standards	USGS Lab,[e] Mixed standards in 0.1 N HNO_3	Mixed standard in H_2O	Hydride generation	Commercial[h] laboratory	Mixed standard in[b] 10% HCl	Simulated soil[b] digest[a]	Lubricating oils[i] diluted 1:10 with MIBK
Lu	--	8	--	--	10	--	--	--	--	--
Hf	10	10	--	--	--	--	--	--	--	--
Ta	2	70	--	--	--	--	--	--	--	--
W	0.7	2	1	--	--	--	--	--	--	--
Re	--	--	--	--	--	--	--	--	--	--
Os	--	--	--	--	--	--	--	--	--	--
Ir	--	--	--	--	--	--	--	--	--	--
Pt	80	80	--	--	--	--	--	--	--	--
Au	40	40	--	--	--	--	--	--	--	--
Hg	1	200	1	--	--	--	--	20	200	--
Tl	--	200	--	--	--	--	--	--	--	--
Pb	2	8	2	10	300	--	200	30	70	--
Bi	50	50	--	--	--	0.8	--	--	--	--
Th	--	3	--	--	--	--	5	--	--	--
U	30	30	--	--	--	--	--	--	--	--

[a] The simulated soil digest contains 10% HCl and the following elements at the concentrations shown (mg/l) (Al = 1500, Fe = 500, K = 400, Ca = 200, Na = 200, Mg = 100, Ti = 60, Mn = 20, P = 15)
[b] Workman (1979)
[c] Fassel and Kniseley (1974)
[d] Boumans and de Boer (1973)
[e] Garbarino and Taylor (1979)
[f] Nikdel (1979)
[g] Thompson et al. (1978)
[h] Meyer (1979)
[i] Fassel et al. (1976)

limits. The sixth column contains detection limits for the hydride generation technique. Columns 7-10 illustrate detection limits which are achieved during the routine analysis of more complex samples such as lubricating oils and soil digests.

If the data in Table 2.13 are to aid the generalist in selecting an analytical technique, they must be reproducible from one laboratory to the next. That is, a project manager needs to know whether the laboratory to which he is submitting his sample achieves the detection limits commonly cited for ICP spectroscopy. One method of describing the interlaboratory consistency of detection limits is to ratio the highest to the lowest detection limit reported by the different laboratories for each element. A ratio of one then implies perfect consistency, while a ratio of 1000 implies poor consistency. The results of this operation are summarized in Figure 2.4. Here the ratios for columns 1-5 are shown separately as an indication of the "best-achievable" limits. The ratios for all columns (excluding those for the hydride generation procedure) are an indication of the degree to which detection limits are degraded during the routine analysis of complex samples.

Figure 2.4 illustrates that for the studies cited in Table 2.13 the detection limits for the routine analysis of complex samples are significantly poorer than for pure solutions. One reason for this discrepancy is practical. An analytical services laboratory would seldom encounter samples containing sub-ppb levels of major elements such as Na, Mg, and Ca. They would therefore purposely select less sensitive lines so as to successfully monitor the higher concentrations of these elements. In fact, many of the highest ratios in Figure 2.4 are for elements which normally occur well above even the highest detection limit shown in Table 2.13.

Spectral interferences, which are more prevalent for complex samples, also can degrade detection limits and may account in part for the effect shown in Figure 2.4. While interfering lines can be partially

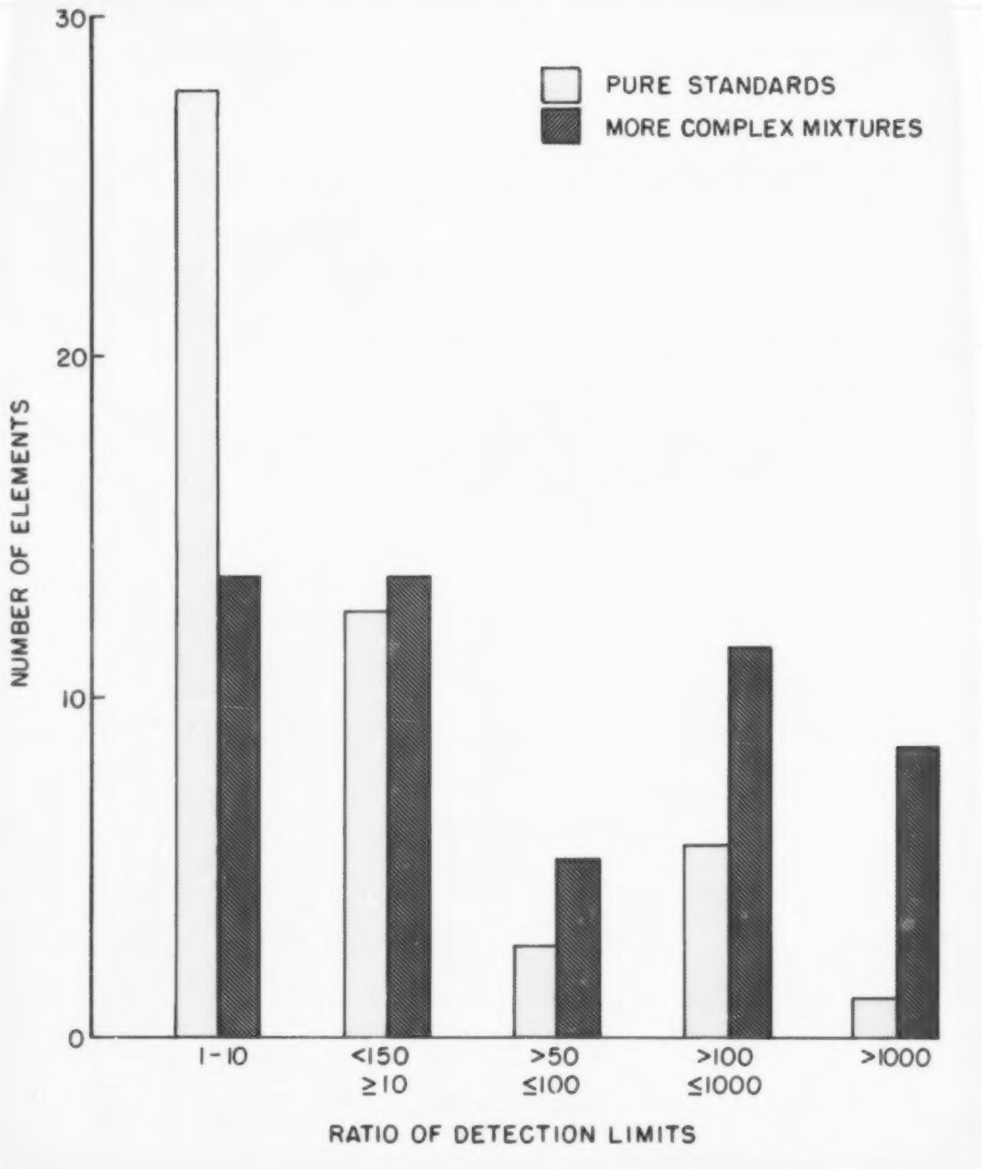

FIGURE 2.4. THE CONSISTENCY OF ICP DETECTION LIMITS

compensated for, their presence nevertheless leads to poorer detection limits.

It must be added that the extent to which "best-achievable" detection limits can be transferred to complex samples is still being debated in the literature (Garbarino and Taylor, 1979; Fassel and Kniseley, 1974). For example, spectral interferences are common in ICP spectroscopy and are compensated for by applying a correction to the analyte line in proportion to the concentration of the interfering species. This procedure succeeds only if all possible interfering elements are determined quantitatively, a task which becomes more difficult with increasing sample complexity. Even when spectral interferences are recognized and compensated for, detection limits are nevertheless degraded by their presence, especially when the interfering line is stronger than the analyte line and the final concentration depends on a small difference between two large numbers. In view of the incomplete knowledge of the sample, many analysts therefore quote cautiously high detection limits.

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2.5 Optical Emission Spectroscopy

This section discusses the capability of classical "arc and spark" optical emission spectroscopy (OES). While a wide variety of other emission sources, such as microwave discharges, are of current research interest, the classical "arc and spark" techniques are already available from a large number of commercial and geochemical exploration laboratories. Barnes (1979) summarizes developments in the field of OES for the interested reader.

Advantages of OES include its low cost (currently ∿ $10/sample) and its ability to analyze solid samples directly, or at least after admixture with graphite. The results of most routine OES analyses are reproducible to within a factor of 1.3 to 2.0, depending in part on whether peak intensities are estimated visually or are measured electronically. These features suit OES well for geochemical prospecting, which can tolerate a rather poor precision but which requires analysis of a large number of samples at minimal cost.

Table 2.14 summarizes OES detection limits reported by three laboratories. The values in column 1 are from a commercial laboratory involved in geochemical exploration and as such are representative of a variety of minerals. The second column, from a government geological laboratory, is similarly representative of their experience with silicate rocks. The third column is based on a manufacturer's experience with mixtures of metal oxides in graphite. The detection limits in Table 2.14 were often determined by subjective, visual estimates of peak height rather than by mathematical formulation. Thus, the agreement shown in Table 2.14 is impressive, especially considering variations in spectrometer design and sample composition between the various laboratories. For 61 elements in Table 2.14, detection limits were reported by more than one laboratory. Of these, the detection limits reported by the geochemical laboratories for the major elements Mg, Si, P, Ca, and Fe were 50 to 1000 times higher than those reported by the manufacturer.

TABLE 2.14. DETECTION LIMITS FOR OPTICAL EMISSION SPECTROSCOPY (μg/g)

	Commercial Geochemical Exploration Laboratory	Government Geochemical Laboratory	Manufacturer
Li	--	100	500
Be	2	1	0.1-0.5
B	10	5	2
Na	--	200	500
Mg	200	500	0.2
Al	--	100	10
Si	--	500	1
P	--	500	100
S	--	--	--
K	--	1500	>1000
Ca	200	800	1
Sc	10	1	--
Ti	20	50	10
V	10	1	20
Cr	10	0.5	10
Mn	10	0.1-1.0	5
Fe	500	100	5
Ca	5	0.5	20
Ni	5	1	20
Cu	2	0.5	1
Zn	200	5	50
Ga	10	2	20
Ge	20	1	5
As	500	200	100
Se	--	--	1000
Rb	--	--	>1000
Sr	50	0.5	50
Y	10	1	--
Zr	20	2	50
Nb	20	5	10
Mo	2	1	--
Ru	--	10	100
Rh	--	2	10
Pd	--	1	10
Ag	1	0.5	1
Cd	50	10	20
In	--	50	20
Sn	10	5	20
Sb	100	50	50
Te	--	--	500
Cs	--	--	500
Ba	5	2	5

TABLE 2.14 (continued)

	Commercial Geochemical Exploration Laboratory	Government Geochemical Laboratory	Manufacturer
La	20	5	5
Ce	--	50	1000
Pr	--	70	20
Nd	--	50	20
Pm	--	--	--
Sm	--	50	20
Eu	--	1	5
Gd	--	10	10
Tb	--	50	50
Dy	--	10	5
Ho	--	1000	5
Er	--	5	5
Tm	--	5	5
Yb	--	0.5	1
Lu	--	10	5
Hf	--	100	50
Tu	--	500	--
W	50	50	100
Re	--	50	50
Os	--	20	--
Ir	--	50	50
Pt	--	10	<5
Au	--	5	<5
Hg	--	--	500
Tl	--	5	50
Pb	10	2	20
Bi	10	10	5
Th	--	200	500
U	--	300	500

This apparent discrepancy probably arises because the geochemical laboratories are likely to choose deliberately less sensitive lines for the major elements in order to stay within the dynamic range of their instruments. For the remaining 56 elements, detection limits are within a factor of 20 for all but ten elements. The consistency of the data in Table 2.14 thus suggests its usefulness for judging the applicability of OES.

In spite of the consistency shown in Table 2.14, it must be recognized that the presence of interfering elements, especially in complex samples, frequently degrades detectability by forcing the analyst to use a less sensitive line. Ho, for example, according to Table 2.14, is 200 times more readily detected in graphite than in silicate rock. Examination of the wavelength tables indicates the presence of Fe and Ti spectral lines within 0.02 nm of the most intense Ho lines. The ubiquitous presence of Fe in geological materials thus forces the analyst to use less sensitive lines for Ho. Such situations are frequent in complex samples and may explain in part the variations in Table 2.14.

The detection limits for OES are clearly inferior to those for SSMS, implying that on the average fewer elements will be detected by OES than by SSMS. Nevertheless, when the detection limits in Table 2.14 are adequate, OES provides an inexpensive and rapid elemental survey.

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2.6 Spark Source Mass Spectroscopy

In spark source mass spectroscopy (SSMS) ions are generated from a solid sample through the action of a radiofrequency spark and are separated and detected in a mass spectrometer. Quantitative analysis is possible because the intensity of the various ions is proportional to elemental concentrations in the sample.

SSMS is unique in its ability to detect every element with nearly uniform sensitivity during a single analysis. However, although detectable, many elements may not be detected with reasonable accuracy. The gaseous elements (H, N, O, and the noble gases) do not lend themselves to quantitative determination by SSMS. Carbon is difficult at low concentrations due to its presence in the residual vacuum and because it is a frequent choice for depositing solutions for analysis. Hg may volatilize during the sparking process and therefore is not normally reported. However, the remaining elements can be detected to levels of approximately 1 ng/g, although a detection limit of 0.1 to 1.0 μg/g is more common for the routine analyses of solids. The precision of SSMS can vary from 2 to 50% depending on the sample and the exact analytical procedure. Variations in SSMS analyses which affect detectability, precision, and accuracy include the following:

- electrode preparation procedures
- sample digestion and ashing procedures, if required
- resolving power of the mass spectrometer
- the sample: interferences, volatile elements, hydrocarbons

- automatic spark gap control

- the sample: interferences, volatile elements, hydrocarbons

- data interpretation procedures: visual vs densitometric, computerized vs manual

These factors will each be treated in turn.

Samples for SSMS must be introduced to the mass spectrometer in the form of solid, non-volatile conducting electrodes. Non-conducting solids are normally mixed with a conducting powder such as graphite and are pressed into a solid electrode. Similarly, water samples are slurried with graphite, gently dried or lypholized, and compacted into electrodes. For normal surface and groundwater the latter procedure can result in a thousand-fold concentration of the sample. Since the sparking procedure consumes only a few mg, with either solids or liquids the degree of homogenization of the electrode material is a major factor determining the ultimate precision of the analysis.

Additional electrode preparation techniques are available for enhancing detectability. For example, elements in solution can be electro-deposited into a conducting material such as gold, which then serves as an electrode. Alternately, small samples can be compacted into the tip of an electrode, permitting the ppm level analysis of only a few mg of material.

High levels of hydrocarbons in a sample produce ions at essentially every mass-to-charge ratio, thereby obscuring trace element peaks. Samples such as oils and biological materials therefore require chemical or thermal decomposition prior to analysis. This can often be accomplished by mixing the sample with a graphite powder and heating to 450°C, which is often adequate to decompose organic compounds but not graphite. This procedure is convenient but may permit the volatilization of certain trace elements such as S or Se. Boron in acidic solution may also be lost, as well as organic halides and volatile organometallic complexes. This problem can be minimized by combusting the sample in a quartz-lined oxygen bomb in the presence of nitric acid. The residue is then slurried with graphite and compressed into an electrode.

Lower levels of hydrocarbons and organic compounds are usually tolerable. For example, coal, which has a low H content, can be analyzed with no ashing. It is not clear at this time whether oil shale, with a higher H:C ratio, could also be analyzed directly.

To a first approximation the mass spectrum includes only singly charged, mono-atomic ions. However, doubly-charged and polymeric ions, as well as hydrocarbon ions, do occur and can mask nearby trace element peaks. For example, $^{54}Fe^{2+}$ falls at the same nominal mass-to-charge ratio (m/q) as ^{27}Al. In this case the m/q ratio of $^{27}Al^{+}$ is 26.98154 while that of $^{54}Fe^{2+}$ is 26.96980. Most of the newer spark source mass spectrometers can resolve the mass difference between $^{27}Al^{+}$ and $^{54}Fe^{2+}$ as well as similar interferences, although this achievement was difficult for the original models. Having the best possible resolution becomes increasingly important with complex environmental samples. Spectral resolution is therefore an important variable in determining the number of elements which can be successfully detected.

Many spark source mass spectrometers are equipped for either photographic or electrical detection. However, the best resolution (~ 10,000) is possible only with photographic detection, while a resolution of 500 is typical of electrical detection. Photographic detection is required to resolve a number of interferences which occur in complex environmental samples, and is therefore normally the method of choice for the routine analyses of uncharacterized samples.

The photographic plate records a mass range of 40:1 (U-238 to Li-6) simultaneously. A detection limit of approximately 1 ng/g is possible for most elements by prolonged exposure, although a limit of approximately 0.1 μg/g is more typical of routine analyses. The precision achieved with photographic detection is in the range of 30-40% for routine analyses.

Considerably better precision is possible with electrical detection operated in the peak switching mode. (A selected list of peaks is focused sequentially into the electron multiplier by stepping the ion accelerating voltage.) Using this approach, Morrison and Colby (1972) achieved a precision (1σ) of 2% for homogeneous samples. This unusually good value was obtained by instrumentally controlling the spark voltage and electrode gap, and represents the minimum instrumental error which can be expected.

Electrical detection may also be operated in the scanning mode by allowing the magnetic field to decay continuously, thereby scanning the entire mass spectrum. This mode provides a rapid elemental survey but cannot distinguish interfering peaks as well as the photographic detection. Thus, selection of the method of detection inevitably involves a compromise between precision, speed of analysis, and the number of elements which can be detected free from interferences.

Finally, some samples are obviously better suited than others for SSMS. For the reasons discussed previously in this section, conducting or semiconducting solids are ideal and can be analyzed with no sample manipulation other than cutting and etching. Other materials require some type of ashing, drying, or sample manipulation, which raises the possibility of sample loss or contamination. Spectral interferences also depend on the sample but are best evaluated on a case-by-case basis.

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2.7 Atomic Absorption Spectroscopy

In this section atomic absorption spectroscopy (AAS) is used generically to include absorption, emission, and fluorescence techniques. Because familiarity with AAS techniques is widespread, I do not attempt to review this technology here, but rather simply list common variations which affect its precision, range, and accuracy.

- Instrument Design and Manufacturer. This is normally a minor influence for most instruments found in testing laboratories. Exceptions include limited-purpose instruments, such as clinical spectrometers devoted to measuring Na in serum, and developmental instruments embodying new design concepts, such as Zeeman background correction.

- Background Correction. Continuous background correction, normally accomplished with a broadband D_2 light source, may either degrade or improve precision. It becomes increasingly desirable with decreasing levels of analyte and increasing levels of concomitant salts.

- Detection Mode. Whether an element is measured by atomic fluorescence, absorption, or emission, changes its detectability several orders of magnitude. Spectral interferences may become more important in atomic emission.

- Atomization Process. The manner by which the analyte is converted into gaseous atoms is a major consideration. Carbon rod techniques are often 10-100 times more sensitive than flame techniques.

The chemical generation of Hg vapor (cold vapor technique) improves detectability over 1000 times compared to flame atomization. Introducing elements such as Se, As, Sb, and Te as the gaseous hydride may improve their detectability by over 100 times in comparison to direct aspiration into a flame (Jackwerth et al., 1979), but often at a cost of degraded precision. Additional modifications of the atomization process are available in the literature.

- Sample Characteristics. Samples which contain high salt content may generate excessive spectral background and require dilution. Interfering chemicals may form stable compounds with the analyte in the flame, thereby adversely affecting accuracy.

- Enrichment Procedures. Detectability can often be improved by concentrating the analyte prior to analysis. Examples include extracting the analyte into an organic solvent or simply evaporating part of the sample.

- Contamination Problems. Achieving the ultimate detectability for very common elements such as Na may require clean rooms and specially purified reagents.

Additional factors affecting the performance of AAS are reviewed by Hieftje and Copeland (1979).

Unlike INAA and XRF, detection limits for AAS cannot be calculated a priori but are determined experimentally. Table 2.15 lists such limits for both flame and carbon rod techniques as described by the EPA methods manual and by the manufacturer's literature. Here detection limits are approximately two times the background noise level. The working limits shown in the table are the lowest concentrations typically reported by a commercial analytical services laboratory located in Denver. In this case the working limits are usually set at several times the detection limits which can be obtained by that laboratory in order to avoid reporting imprecise analyses. The working limits in this table are also based on the requirements of water quality regulations, economics, reagent contamination levels, and ease of operation. For the sake of comparison the final column in Table 2.15 also lists quality criteria for surface waters in Colorado.

Several features of Table 2.15 deserve comment. First, carbon rod detection limits are usually ten to 100 times better than flame detection limits. Second, the manufacturer's detection limits are often five times lower than those listed in the EPA manual. This amount of variation between laboratories is not unusual and may represent in part the EPA's experience with ground and surface waters and the manufacturer's experience with pure solutions. Third, the working limits of the commercial laboratory are usually in the range of the detection limits cited from the other two sources, implying that such limits are indeed realistic for surface and ground waters. In the commercial laboratory most elements are determined by flame rather than carbon rod AAS because this mode is less time consuming and is adequate for most applications. However, it is also apparent that detectability could be improved for most elements by using carbon rod atomization or sample preconcentration if so requested by the customer. (In situations where AAS detection limits are inadequate, the alternate techniques are listed in Table 2.15.) Fourth, in contrast to INAA and XRF, detection limits for AAS are normally lower than the lowest water quality criteria. Fifth, a comparison of Tables 2.13 and 2.15 illustrates the complementary nature of ICP spectroscopy and AAS for water analysis. Elements such as Se and As, which are only poorly detected by ICP, are easily detected by AAS. The opposite holds true for refractory elements such as B, P, W, Zr, Nb, and U, which are much more readily detected by ICP spectroscopy than by AAS.

TABLE 2.15. DETECTION LIMITS FOR ATOMIC ABSORPTION SPECTROSCOPY. All values are in µg/l.

	Detection Limit				Working Limit		Colorado Water Quality Standards Cleanest Classification
	EPA Method Manual		Manufacturer's Literature		Commercial Laboratory		
	Flame	Carbon rod	Flame	Carbon rod			
Li	--	--	2	0.4	5	f	--
Be	5	0.2	0.7	0.2	5	f	10
B	--	--	2000	--	50	d	750
F	--	--	--	--	100	p	--
Na	2	--	0.2	0.02	100	f	--
Mg	1	--	0.2	0.006	50	f	125000
Al	100	3	20	2	100	f	100
Si	--	--	200	7	1000	d	--
P	--	--	--	--	100	d	--
Cl	--	--	--	--	200	d	--
K	10	--	2	0.2	100	f	--
Ca	10	--	2	0.06	50	f	--
Sc	--	--	30	--	--	--	--
Ti	400	10	50	--	300	f	--
V	200	4	50	10	5	f	--
Cr	50	1	5	0.5	10	f	50
Mn	10	0.2	2	0.04	5	f	50
Fe	30	1	6	0.5	10	f	300
Co	50	1	7	0.8	10	f	--
Ni	40	1	8	1.0	10	f	50
Cu	20	1	2	0.4	10	f	10
Zn	5	0.05	1	0.02	5	f	50
Ga	--	--	40	2.0	--	--	--
Ge	--	--	100	--	--	--	--
As	2[b]	1	2[b]	15	2	r	50
Se	2[b]	2	2[b]	6[b]	5	r	--
Rb	--	--	2	0.6	--	--	--
Sr	--	--	2	0.8	10	f	--
Y	--	--	100	--	--	--	--
Zr	--	--	1000	--	--	--	--
Nb	--	--	3000	--	--	--	--
Mo	100	1	30	0.6	5	r	--
Ru	200	20	90	--	--	--	--
Rh	50	5	5	--	--	--	--
Pd	100	5	20	3	--	--	--
Ag	10	0.2	2	0.3	0.05	r	0.1
Cd	5	0.1	0.7	0.02	2	f	0.4
In	--	--	40	6	--	--	--

TABLE 2.15 (continued)

	Detection Limit				Working Limit		Colorado Water Quality Standards Cleanest Classification
	EPA Method Manual		Manufacturer's Literature		Commercial Laboratory		
	Flame	Carbon rod	Flame	Carbon rod			
Sn	800	5	30	1.0	500	f	--
Sb	200	3	40	3.0	50	f	--
Te	--	--	40	--	--	--	--
Cs	--	--	4	4.0	--	--	--
Ba	100	2	20	2.0	50	f	1000
La	--	--	2000	4000	--	--	--
Ce	--	--	--	--	--	--	--
Pr	--	--	8000	--	--	--	--
Nd	--	--	1000	160	--	--	--
Pm	--	--	--	--	--	--	--
Sm	--	--	800	60	--	--	--
Eu	--	--	10	7	--	--	--
Gd	--	--	1000	--	--	--	--
Fb	--	--	500	360	--	--	--
Dy	--	--	30	8	--	--	--
Ho	--	--	40	40	--	--	--
Er	--	--	30	8	--	--	--
Tm	--	--	10	2	--	--	--
Yb	--	--	2	0.6	--	--	--
Lu	--	--	300	--	--	--	--
Hf	--	--	1000	200	--	--	--
Ta	--	--	2000	--	--	--	--
W	--	--	500	16000	--	--	--
Re	5000	200	900	800	--	--	--
Os	300	20	100	--	--	--	--
Ir	3000	30	400	--	--	--	--
Pt	200	20	90	10	--	--	--
Au	100	1	9	1	--	--	--
Hg	0.2[c]	--	0.04[c]	12	0.02	c	0.05
Tl	--	--	10	0.6	5	r	15
Pb	100	1	20	0.3	1	r	4
Bi	--	--	50	1	500	f	--
Th	--	--	--	--	--	--	--
U	--	--	60000	1000	2	g	30

TABLE 2.15 (continued)

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[a] Working limits correspond to several times the background noise level and are based on a wide variety of ground and surface waters using equipment routinely. Detection limits correspond to approximately two times the background noise level.

[b] gaseous hydride method

[c] cold vapor technique

[d] colorimetric

[f] flame atomic absorption

[r] carbon rod (flameless) atomic absorption

[g] fluorometric

[p] potentiometric (ion selective electrode)

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2.8 Applications

The number of reports on the role and concentrations of trace elements is obviously too large to summarize here. I have rather selected a few representative studies to illustrate the interplay between the various multi-elemental techniques discussed above. Tables 2.16 and 2.17 summarize the success of these techniques when applied to geological materials, oil shale, wastewaters, and oils. These tables indicate only those elements successfully measured at levels above the detection limit in a variety of samples, and refer the reader to the original articles for detailed descriptions.

It is apparent from Tables 2.16 and 2.17 that almost every element in the periodic table can be successfully determined in many environmental samples using the techniques listed. The exceptions to this statement are the environmentally-important light elements H-F, P, and S. For these elements, specialized techniques are often required which have not been discussed in this chapter.

TABLE 2.16. AN INDEX TO STUDIES EMPLOYING MULTIPLE TECHNIQUES FOR ELEMENTAL ANALYSIS OF SOLID ENVIRONMENTAL SAMPLES

	NAA	XRF	ICP/PES	OES	SSMS	AAS
H						
He						
Li	U			U	U	U
Be				U,W		U
B			X	U	U	
C						
N						
O	U	U			U	
F	U			U	U	
Na	U,X	U		U	U	U,X
Mg	U	U	X	U	U,W	U,X
Al	U,X	U	X	U	U,W	U,X
Si	U	U,X		U	W	U,X
P	U	U			U	
S	X	U,W,X		W		
Cl	U	U			U	
K	U,X	U,W,X	X	U	U,W	U,X
Ca	U,X	U,W,X	X	U	U,W	U,X
Sc	U,X	U		U		
Ti	U,X	U,W,X	X	U	U,W	U,X
V	U,X	U,X	X	U	U,W	U,W
Cr	U,X	U,X	X	U	U,W	U
Mn	U,X	U,W,X	X	U	U,W	U
Fe	U,X	U,X	X	U,W	U,W	U,X
Co	U,X	U		U,W	U,W	U
Ni	U,X	U,X	X	U,W	W	U,W
Cu	U	U,X	X	U	U,W	U
Zn	U,X	U,X	X	U,W	U,W	U,X,W
Ga	U	U,X		U	U	
Ge	U			U	U	
As	U,X	X			W	W
Se	U,X				U,W	W
Br	U,X					
Rb	U,X	U,X		U	U	U
Sr	U,X	U,X	X	U	U	U,X
Y	U	U,X		U	U	
Zr	U	U,X		U	U	X
Nb		U,X		U	U	
Mo	U	X	X	U	U	U
Tc						
Ru	U				U	
Rh				U	U	
Pd	U			U	U	
Ag	U			U	U	U
Cd	U,X				U,W	U,X,W

TABLE 2.16 (continued)

	NAA	XRF	ICP/PES	OES	SSMS	AAS
In	U			U		
Sn	U			U	U,W	
Sb	U,X				U,W	W
Te	U				U	
I	U				U	
Cs	U,X				U	U
Ba	U,X	U,X	X	U	U	U,X
La	U,X	U		U	U	
Ce	U,X	U		U	U	
Pr	U	U		U	U	
Nd	U,X	U		U	U	
Pm						
Sm	U,X	U			U	
Eu	U,X	U		U	U	
Gd	U	U		U	U	
Tb	U,X	U		U	U	
Dy	U,X	U		U	U	
Ho	U,X	U		U	U	
Er	U	U		U	U	
Tm	U	U			U	
Yb	U,X	U		U	U	
Lu	U,X	U		U	U	
Hf	U,X				U	
Ta	U,X					
W	U			U	U	
Re	U				U	
Os	U				U	
Ir	U				U	
Pt	U			U		
Au	U					
Hg	U					U,X
Tl	U			U	U,W	W
Pb		U,X		U,W	U,W	U
Bi	U			U	U,W	
Po						
Ac						
Th	U,X	U		U	U	
Pa						
U	U,X			U	U	

U : USGS standard rocks (Flanagan, 1976)
V : omega-9 wastewater (Fox et al., 1978)
W : fly ash (Davison, 1974)
X : spent and raw oil shale, shale oil, wastewaters (Fruchter et al., 1979)
Z : USGS water (Ronan et al., 1977)

TABLE 2.16 (continued)

NAA :	Neutron activation analysis, including both radiochemical and instrumental versions
XRF :	X-ray fluorescence
ICP/PES :	Inductively coupled plasma and plasma emission spectroscopy.
OES :	"Arc and spark" optical emission spectroscopy
SSMS :	Spark source mass spectrometry
AAS :	Atomic absorption spectroscopy, including flame, cold vapor, and carbon rod methods

TABLE 2.17. AN INDEX TO STUDIES EMPLOYING MULTIPLE TECHNIQUES FOR ELEMENTAL ANALYSIS OF LIQUID ENVIRONMENTAL SAMPLES

	NAA	XRF	ICP/PES	OES	SSMS	AAS
H						
He						
Li			X	V		V,X
Be						
B			V,X,Z	V		V
C						
N						
O						
F						
Na	V,X					V
Mg	X		V,X,Z			V,X
Al	V		Z		V	
Si			V,X		V	V,X
P			V,X		V	
S	X					
Cl	V,X					
K	X					V,X
Ca		V	V,X,Z			X
Se	V					
Ti		V,X		V	V	V
V	X	V	V,X	V	V	
Cr			Z	V	V	
Mn	V,X	V	X,Z	V	V	X
Fe	V	V,X	Z	V	V	V
Co	X	V	Z	V	V	
Ni	V,X	V,X	Z		V	
Cu	V	V,X	V,Z		V	V,X
Zn	V,X	V,X	V,X,Z		V	V,X
Ga					V	
Ge					V	
As	V,X	V,X	V,X		V	V
Se	V,X	V,X	X		V	V
Br	V	V			V	
Rb	V,X	V,X		V	V	
Sr	V,X	V,X	X	V	V	
Y					V	
Zr		V		V	V	
Nb					V	
Mo	V	V	V,X,Z	V	V	
Tc						
Ru						
Rh						
Pd						
Ag	V		Z		V	V
Cd					V	V

TABLE 2.17 (continued)

	NAA	XRF	ICP/PES	OES	SSMS	AAS
In						
Sn					V	V
Sb	V,X			V	V	V
Te					V	
I					V	
Cs						
Ba		V	V,X	V	V	
La					V	
Ce	V				V	
Pr					V	
Nd						
Pm						
Sm						
Eu						
Gd						
Tb						
Ry						
Hc						
Er						
Tm						
Yb						
Lu						
Hf	V				V	
Tu					V	
W					V	
Re						
Os						
Ir						
Pt						
Au						
Hg						VX
Tl						
Pb			Z	V	V	
Bi						
Po						
Ac						
Th	V					
Pa						
U	V	V			V	

U : USGS standard rocks (Flanagan, 1976)
V : omega-9 wastewater (Fox et al., 1978)
W : fly ash (Davison et al., 1974)
X : spent and raw oil shale, shale oil, wastewaters (Fruchter et al., 1979)
Z : USGS water (Ronan et al., 1977)

TABLE 2.17 (continued)

NAA :	Neutron activation analysis, including both radiochemical and instrumental versions
XRF :	X-ray fluorescence
ICP/PES :	Inductively coupled plasma and plasma emission spectroscopy
OES :	"Arc and spark" optical emission spectroscopy
SSMS :	Spark source mass spectrometry
AAS :	Atomic absorption spectroscopy, including flame, cold vapor, and carbon rod methods

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3.0 WASTEWATERS

Before analyzing a wastewater it is helpful to have some idea of materials that may be present. With this initial insight the analyst can then develop realistic chemical standards with which to calibrate and test his methods. He can anticipate what peripheral reactions may occur during sample handling and analysis, and thereby lessen the likelihood of unexpected interferences. Most importantly, he can develop and apply those methods which are most accurate and interference free for the type of sample in hand.

Table 3.1 lists some of the major wastewater streams associated with the Paraho, TOSCO II, and modified in situ retorting plants. (See Nevens et al. [1979] for a more detailed description of waste volumes and flow schemes.) In this table, and throughout the text, waters produced in the retorting section of an oil shale plant--as opposed to waters produced elsewhere in the plant--are referred to as retort waters. The analysis of groundwaters, river water and sanitary wastes are treated extensively elsewhere and will not be treated further here. In addition, the concentrate from the reverse osmosis treatment should be amenable to standard methods of analysis, at least after dilution to its original concentration. As is apparent from this table, there remain several process streams requiring analysis.

Table 3.2 describes the retort waters associated with various processes. Significant variations are apparent and can be explained, although all the retort waters shown are primarily a solution of ammonium carbonate and bicarbonate.

TABLE 3.1. MAJOR WATER STREAMS ASSOCIATED WITH OIL SHALE PROCESSES (Complete water balances and flow schemes are given by Nevens et al. [1979])

PARAHO
DIRECT MODE

River water
Potable water
Raw and digested sanitary wastes
Runoff from plant & spent shale pile
Gas condensate
Gas condensate stripped of acid gases & NH_3
Gas condensate after organic digestion
Cooling tower makeup & blowdown
Boiler water makeup & blowdown
Leachate from raw and spent shale

TOSCO II with
Partial Refining

As above with addition of:
Gas refining & coking wastes
Wastes from oil hydrogenators
Wastes from NH_3 separator
Miscellaneous wastes from refinery

Modified
In Situ

As above, with addition of:
Condensate/leachate from bottom
  of retort ("drippings")
Excess groundwater
  treatment of groundwater

TABLE 3.2. THE COMPOSITION OF RETORT WATERS ASSOCIATED WITH VARIOUS PROCESSES

	Paraho Recycle Gas[a] Condensate			
Cations	Direct Mode	Indirect Mode	TOSCO II[b]	Omega-9[d] In Situ
Ca^+	61	39	6	12
Mg^{++}	<0.1	<0.1	2	20
Na^+	0.2	0.29	5	4,300
K^+	0.08	0.18	0.4	50
$NH_3{}^+$	5,700	13,600	5,200	3,470
Anions				
$CO_3^=$	24,000	2,400		500
HCO_3^-	26,000	5,500		16,000
$SO_4^=$	110	1.7		2,000
$S^=$	<0.1	390	760	~0
Cl^-	TR	TR	5	
F^-	0.35	0.1	0.3	
NO_3^-	120	1.0		0.2
$HCO_3^- + CO_3^=$ as CO_2			6,200	12,000
CN^-			~20	~1
$S_2O_3^=$	(0.1-10)[c]			2,700
PO_4^{3-}				0.08-25
SO_3^{2-}				<20
$S_4O_6^=$				300
SCN^-				120

TABLE 3.2 (continued)

	Paraho Recycle Gas[a] Condensate			
Other Inorganics	Direct Mode	Indirect Mode	TOSCO II[b]	Omega-9[d] In Situ
NH_3-N	19,400	29,600		3,100
TKN	31,400	-		3,420
Total P	0.6	0.8		3
Total S			810	2,010
B				
Non-Specific Parameters				
BOD	12,000	4,850		740
COD	19,400	17,100		
TOC	29,200	9,800		
TIC	9,800	1,600	1,700	3,300
Oil & grease	500	30		600
Total solids (upon evaporation)	22,000	400		14,000
Total suspended solids	200	-		
Alkalinity	69,000	13,000		
pH	9.8	9.5	8.9	8.6
Total S			810	
Conductivity (mmho/cm)				~19

TABLE 3.2 (continued)

Organic Materials	Paraho Recycle Gas[a] Condensate Direct Mode	 Indirect Mode	TOSCO II[b]	Omega-9[d] In Situ
Phenolic compounds	46	42	10,000	60
Extractable & nonvolatile:				
Neutrals	94	420	3,000	
Acids	87	220	4,200	
Bases	21	50	1,300	
BOD	12,000	4,850		
COD	19,400	17,100		8,100
TOC	29,200	9,800		1,000
Organic N				100-600
Volatile acids				
DOC			6,100	1,000[e]
Hydrophobic Bases				130[e]
" Acid				190[e]
" Neutrals				
Hydrophilic Bases				120[e]
" Acids				290[e]
" Neutrals				

---

[a] Prien et al. (1977)

[b] Haas (1979)

[c] Wildeman and Hoeffner (1979), during a different sampling period

[d] Fox et al. (1978)

[e] Stuber and Leenheer (1979)

The TOSCO II retort water was condensed outside of the retort, so that the liquid did not contact the shale. As would be expected, the content of non-volatile species, such as Na, Ca, and $SO_4^=$ is lower than in the other retort waters. Sulfur is present mainly as $S^=$, as is reasonable for an anaerobic retorting process.

The omega-9 water, on the other hand, condensed in the in situ retort in contact with the surrounding raw and retorted shale. In addition, this water supposedly contains a great deal of the surrounding groundwater which may explain the lower levels of NH_3. (NH_3 is produced almost entirely by the retorting operation and is essentially absent in local groundwaters.) Na^+ and $SO_4^=$ are readily leached from spent shale, and these species constitute a major fraction of the dissolved salts in this sample. Unlike the TOSCO II retort water, in the omega-9 water S is present mainly as sulfur oxides such as $S_2O_3^=$, $S_4O_6^=$ and $SO_4^=$, consistent with the more oxidizing atmosphere expected in any retorting process using direct air injection.

The two waters collected from the Paraho retorts cannot be compared directly because of the lack of retort operating data. In addition, ion balances for both Paraho samples are sufficiently unequal so as to raise questions regarding the completeness of the analyses. The data is included to indicate the range of values expected from different retorts.

All the retort waters shown contain dissolved organic carbon as a major component. Comparison of the nonvolatile organic carbon and the TOC values for the Paraho retort waters suggests a high content of volatile organic compounds.

Although retort waters have been the most widely discussed in the literature, effluents from the hydrogenation units associated with the partial refining operation and "blowdown" from the cooling towers may constitute larger streams. Samples of such waters are not now available for analysis. In any case, it is clear that analytical methods which are developed in the future must be suited for a wide range of samples. Methods which solve problems specifically associated with retort waters but which lack broad applicability may be of limited use.

3.1 Reactions and Equilibria

Several of the major species in retort waters undergo acid-base reactions, and these waters should therefore be highly buffered. The pK_a values for a few representative species are shown below:

	pK_a
HCO_3^-	10.3
$H_2O \cdot CO_2$	6.4
NH_4^+	9.3
Organic Acids	
acetic, butyric	4.8
benzoic	4.0
Organic Bases	
methylamine	10.7
aniline	4.6
pyridinium	5.2

(I do not imply here that the specific organic compounds are necessarily major components of retort waters, but rather I have included representative examples from the various organic groups which are present in some retort waters as major components.)

The presence of such buffering compounds has several implications for the analyst. In normal surface waters, titratable base is usually attributed to $HCO_3^{=}$ and $CO_3^{=}$. The interpretation of titration curves from retort waters obviously requires much more care and will be discussed further in this chapter. Another complication arises because adjusting the pH of retort waters in either direction should alter the composition.

At low pH organic acids should separate, CO_2 should evolve, and if $S_2O_3^=$ is present, elemental S should precipitate. At higher pH values, NH_3 and possibly some organic amines should escape. These reactions are important because sample preservation and analytical techniques often include pH modification.

Another major feature affecting chemical analysis is the high ionic strength of retort waters. For example, a solution containing 50 g/l of $(NH_4)HCO_3$ and no other component has an ionic strength of 0.63, corresponding to activity coefficients of 0.86 and 0.56 for univalent and divalent ions respectively. Equilibria calculations should therefore take ionic strengths into account for quantitative results. (Under these conditions, for example, $CaSO_4$ should be approximately three times more soluble than in pure water.)

The high ionic strength of retort waters also affects the interpretation of electrical conductivity measurements. Since the equivalent conductivity of ions decreases approximately linearly with $\sqrt{C}$, where C is the concentration of the electrolyte, extra care must be taken in relating conductivity measurements to dissolved salt content (Moore, 1962). Conductivity measurements are discussed in section 3.2.

Retort waters which have been in contact with spent shale may be saturated with respect to extractable minerals, so that changes in temperature, partial pressure, or pH may cause precipitation. For example, the values of Ca and $CO_3^=$ for all the waters shown in the table exceed thermodynamic predictions by up to 1000 fold. As Fox (1979) has observed, the precipitation of $CaCO_3$ can be caused by simply filtering the water.

The high levels of organic compounds raise the possibility that some transition-series metals may be kept in solution as organometallic complexes. These may readily precipitate if the sample is diluted with water.

Several analytical schemes require the complete chemical oxidation or reduction of a water sample prior to analysis. Retort water contains several major species, such as $S^{=}$, $S_2O_3^{=}$, and NH_3, which are readily oxidized, and these species may act as "redox buffers". Because of these redox buffers, the desired species may not be oxidized or additional oxidation reagents may be required.

One instance in which redox buffering may be important is the wet-chemical determination of total S, which begins by oxidizing other S forms to $SO_4^{=}$ using H_2O_2 or Br_2 (AOAC, 1970; APHA, 1955). The quantitative oxidation of NH_3 is thermodynamically favored with either reagent according to the reactions:

$$2NH_3(aq) + 3\ Br_2(l) \rightarrow N_2\ (g) + 6H^+ + 6Br^- \qquad \log K \cong 100$$
$$2NH_3(aq) + 3\ H_2O_2(aq) \rightarrow 6H_2O + N_2 \qquad \log K \cong 160$$

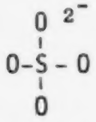
although neither reaction has been confirmed in retort waters (NBS, 1952; Latimer and Hildebrand, 1951). Dissolved organic materal may also have to be oxidized before retort water analysis can proceed. In summary, the successful oxidation of the various S forms in retort water may require more reagent mass and a larger reaction time than is required for ground and surface waters, and similar considerations apply to other analyses which are based on oxidation or reduction processes.

Of particular interest in retort waters is the sulfur/sulfur oxide system containing species such as $S_2O_3^{=}$, $S_4O_6^{=}$, SCN, and $SO_4^{=}$. Species in this system readily interconvert, generate unwanted peripheral reactions during the chemical analysis of unrelated species, form precipitates over a period of several months, and generally make life more complicated for the analyst. Below, some of the more important reactions are discussed. For a more complete review, the reader is referred to Meyer (1977) and Luthy et al. (1977). To facilitate the following discussion, Table 3.3 lists the names of the more common species. Table 3.4 summarizes a few of the reactions which could be expected in retort waters during collection, storage, or chemical analysis.

Under equilibrium conditions, only the species $SO_4^=$, HSO_4^-, S^0, H_2S, and HS^- can exist in water solution in the pH range 1-14. Figure 3.1 illustrates the stability range for each species as a function of pH and Eh (Garrels and Christ, 1965). Clearly, the sulfur/sulfur oxide system found in certain retort waters is thermodynamically unstable, and Figure 3.1 represents only the point of final equilibrium. Reactions of the sulfur/sulfur oxide system which may occur in retort water are described in the following paragraphs.

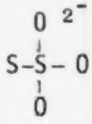
TABLE 3.3. NOMENCLATURE FOR SULFUR/SULFUR OXIDE COMPOUNDS

Structures are illustrated for mnemonic purposes only and do not necessarily represent actual bonding.



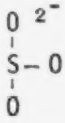
$$\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Sulfate



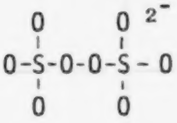
$$\mathrm{S{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Thiosulfate



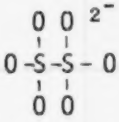
$$\mathrm{\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Sulfite



$$\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}O{-}O{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Peroxydisulfate

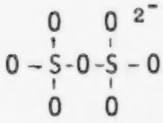


$$\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Dithionate

S^{2-}

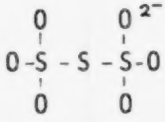
Sulfide



$$\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}O{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Disulfate

pyrosulfate



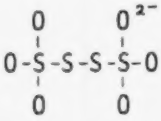
$$\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}S{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Trithionate

$^{-}S{-}S_x{-}S^{-}$

Polysulfide

sulfane



$$\mathrm{O{-}\overset{O}{\underset{O}{S}}{-}S{-}S{-}\overset{O}{\underset{O}{S}}{-}O}^{2-}$$

Tetrathionate

$S{-}O{-}S^{2-}$

Disulfite

CN^{-}

Cyanide

OCN^{-}

Cyanate

SCN^{-}

Thiocyanate

TABLE 3.4. REACTIONS OF THE $S^{=}$ - S° - S_xO_y - CN SYSTEM

(1) $2H_2S(aq) + SO_2(aq) \rightarrow$ Wackenroder's solution $\xrightarrow[\text{months}]{} 2H_2O + \frac{1}{8}S_8^{\circ}$	Wackenroder's solution: HSO_3^-, HS^-, polythionates, polysulfides, elemental S	Meyer (1977)
(2) $S_2O_3^{=} + H^+ \rightarrow \frac{1}{8}S_8^{\circ} + HSO_3^-$	$S_2O_3^{=}$ unstable in mild acids. This reaction is reversible under basic conditions.	
(3) Oxidation of Thiosulfate		
(a) $2S_2O_3^{=} + I_3^- \rightarrow S_4O_6^{=} + 3I^-$	Also with other mild oxidizing agents, pH<5	
(b) $S_2O_3^{=} + 10\ OH^- + 4I_3^- \rightarrow 2SO_4^{=} + 5H_2O + 12I^-$	Basic conditions	
(c) $3S_2O_3^{=} + 26H^+ + 4Cr_2O_7^- \rightarrow 6SO_4^{=} + 8Cr^{3+} + 13H_2O$	Also with other strong oxidizing agents	
(d) $S_2O_3^{=} + 1.86\ O_2 + 1.03\ H_2O + 0.112\ CO_2 + 0.028\ HCO_3^- + 0.028\ NH_4^+ \rightarrow 0.028\ C_5H_7O_2N$ ("cells") $+ 2H^+ + 2SO_4^{=}$	Theoretical biological oxidation	Wang & Mercer (1979)
(4) Cyanolysis of Polythionates:		Kelly et al. (1969)
(a) $S_4O_6^{=} \pm 3CN^- + H_2O \rightarrow S_2O_3^{=} + SO_4^{=} + 2HCN^- + SCN^-$	Spontaneous at low temperatures (5°C) basic solution	
(b) $S_2O_3^{=} + CN^- \rightarrow SO_3^{=} + SCN^-$	Low temperature, basic solution, catalyzed by cupric ions	
(c) $S_3O_6^{=} + 3CN^- + H_2O \rightarrow SO_3 + SO_4^{=} + 2HCN + SCN^-$	Requires high temperature (100°C)	

TABLE 3.4 (continued)

(5) Cyanolysis of Polysulfides		Chen and Morris (1972)
(a) $S^{=} + O_2 \rightarrow S_x^{=}\ ,\ S_8^o$	Rate and final product depends on $S^{=}/O$ ratio, pH, catalytic effects of metal ions and organic compounds	Luthy et al. (1977)
(b) $S_x^{=} + CN^- \rightarrow S^{=} + (x-1)SCN^-$		
(c) $\frac{1}{8}S_8^o + CN^- \rightarrow SCN^-$		

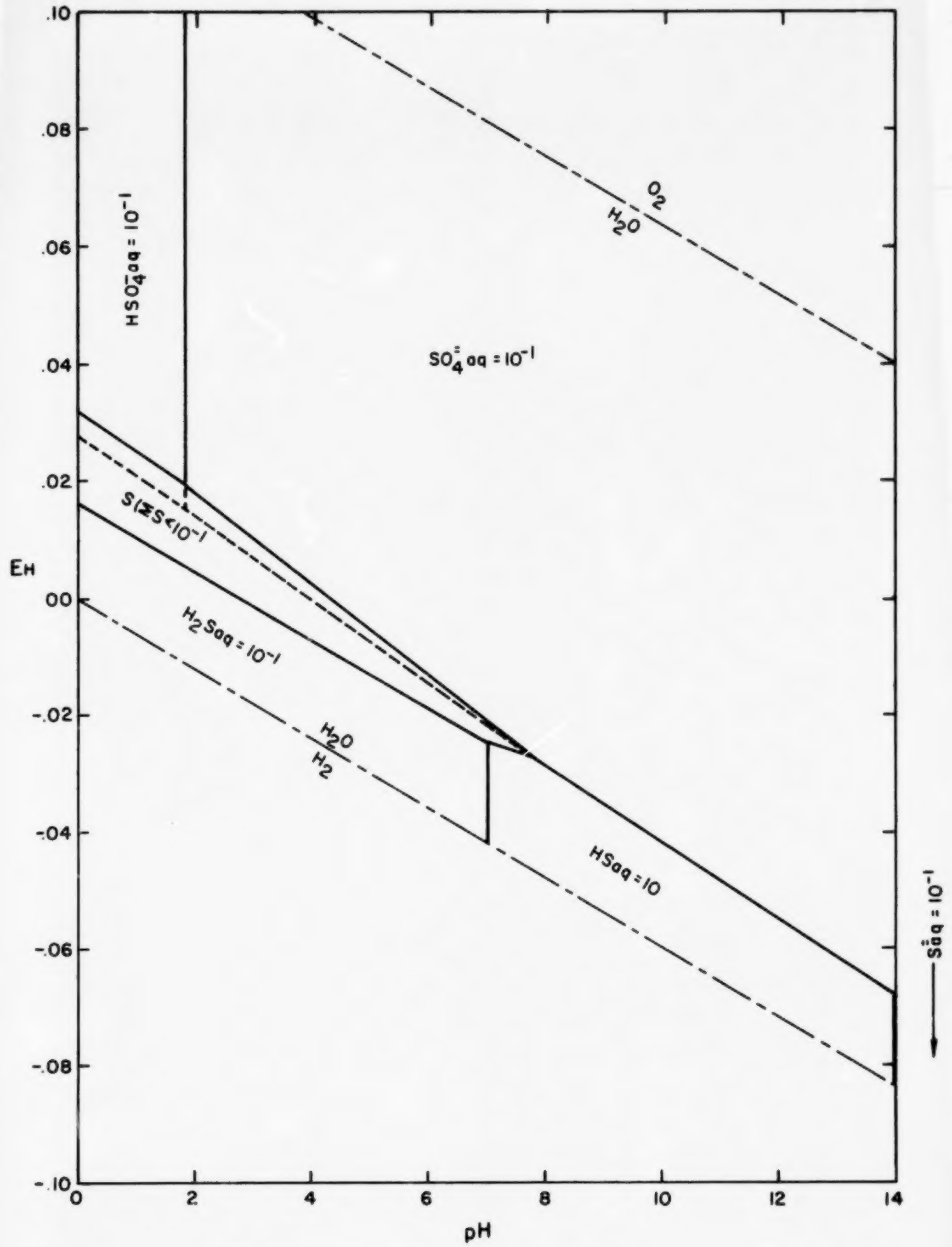


FIGURE 3.1. EQUILIBRIUM DISTRIBUTION OF SULFUR SPECIES IN WATER AT 25°C AND 1 ATMOSPHERE. TOTAL ACTIVITY OF DISSOLVED SULPHUR = 10^{-1}. (REPRESENTED BY PERMISSION. ELSEVIER PUBLISHING COMPANY).

Reactions of H_2S and SO_2 in Water. When SO_2 and H_2S are exposed to water, they form a milky liquid known as Wackenroder's solution, containing suspended sulfur, thiosulfate, bisulfite, polysulfides, and various polythionates. This mixture slowly precipitates S for months.

Although this reaction was first observed by Bertholett almost 200 years ago, much still remains to be known, particularly in the area of kinetics (Meyer, 1977).

This lack of knowledge complicates the task of the analyst considerably. Since the mixture is in a state of disequilibrium, chemical reactions which are designed to isolate one species may change the entire system, perhaps even producing more analyte. Chromatographic separations may not necessarily reflect the original compositions, since reactions can occur during separation. Techniques for sample preservation are similarly complicated.

One cannot help but speculate that the presence of $S_2O_3^=$ in certain retort waters is due to the Wackenroder reaction involving H_2S and SO_2. However, other mechanisms are possible. For example, sulfide reacts with air to form elemental sulfur, which in turn reacts with dissolved SO_2 under basic conditions to form $S_2O_3^=$. (See reactions 2 and 5a in Table 3.4.) This reaction sequence raises the possibility that $S_2O_3^=$ could be generated during sampling and storage.

Reactions of Thiosulfate. Table 3.4 includes several reactions of thiosulfate. Of these, Leenheer has proposed reaction 2 to explain the precipitate which forms upon the acidifications of certain retort wastewaters. The reverse reaction, which occurs under basic conditions, could account for the presence of $S_2O_3^=$. Upon oxidation, thiosulfate yields $S_4O_6^=$, $SO_4^=$ and S° as a side product, depending on the exact conditions (Laitinen, 1960). These reactions are important since they can contribute to BOD and COD measurements and also since they are the basis for the iodometric determination of $S_2O_3^=$ in water. (See reactions 3a-3d in Table 3.4.)

Reactions of Cyanide. The reactions of CN^- to form SCN^- are shown in Table 3.4. Kelly et al. (1969) have used reaction 4a-4c to distinguish the polythionates $S_2O_3^=$, $S_3O_6^=$, and $S_4O_6^=$ in solution. Reactions 4a-5c can be invoked to explain the presence of SCN^- and the absence of CN^- in retort waters, since CN^- would react rapidly to form SCN^-.

In related work on coal gasification wastewaters, which also contain reduced S compounds in a NH_4^+/HCO_3^- matrix, Luthy studied the time dependence of SCN^- and CN^- in stored samples. He found that the CN^- concentration dropped by a factor of 2 within a few hours, and that the SCN^- concentration increased by three fold in 72 hours. It would not be surprising to see similar behavior in some retort waters, at least until the SCN^-/CN^- equilibrium is established. Special care may therefore be required to preserve samples of SCN^- and CN^-.

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3.2 Physical Properties, Conductivity, Dissolved Solids, and pH

The measurement of electrical conductivity, because it is so easily completed, often provides the most readily available, though indirect, indication of total salt concentration. To the plant operator conductivity changes may provide the first clue of changing process conditions; to the agronomist increases in conductivity may be the first indication of degrading water quality. When the major dissolved ions are also determined, conductivity measurements serve a quality assurance function, since the conductivity of dilute solutions varies linearly with ion concentration.

However, at the concentrations of dissolved salts found in retort water conductivity does not necessarily vary linearly with concentration. This complication can easily be avoided by diluting retort waters up to 100x before measuring the electrical conductivity (Wildeman and Hoeffner, 1979). Another advantage of this approach is that the conductivity is then within the range of most commercially available conductivity cells.

Total dissolved solids (TDS) are measured by evaporating a water sample at a specified temperature, normally 103-105°C or at 180°C. For most surface and ground waters TDS measurements are equivalent to total solute content. This procedure gives reproducible but ambiguous results for retort water since major amounts of dissolved gases such as NH_3 and CO_2 also evaporate (Prien et al., 1977; Fox et al., 1978). Thus, for retort water, TDS measurements are not a reliable indicator of dissolved solutes as was originally intended.

One would suppose that TDS values could be corrected to total solute concentrations by adding the concentrations of dissolved CO_2 and NH_3. However, this method has not yet been shown to work uniformly, and there is no reason to assume that dissolved NH_3 and CO_2 will necessarily evaporate quantitatively from every type of retort water. In addition, at least some retort waters lose an unknown fraction of organic material upon heating.

Attempts have also been made to lypholize retort waters in order to measure TDS without loss of NH_3 or CO_2. This approach is attractive because, compared to water, the volatility of NH_4HCO_3 decreases more rapidly with temperature. However, this approach has also failed to avoid the loss of volatile dissolved salts.

Retort waters do not appear to present special difficulties for the measurement of pH. For example, Fox et al. (1978) completed an interlaboratory comparison of pH measurements with three laboratories. They reported a value of 8.65 ± 0.26, a variation typical for the measurement of surface and ground waters.

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3.3 Ion Chromatography

Table 3.5 contains citations describing the principles and recent applications of ion chromatography. As can be seen, most references are dated during the last two years, indicating the increased popularity of this technique. The growth of ion chromatography can be attributed to the introduction in 1975 of commercial instrumentation capable of sensitive multi-species analyses (Small, 1975).

The operating principles of ion chromatography are discussed by Small (1975, 1978) and need not be discussed in detail here. In summary, like other types of ion exchange chromatography, ions are separated on an ion exchange resin in an electrolyte solution. In ion chromatography, the eluent ions are selectively removed in a subsequent "suppressor" column leaving the ionized analyte ions, which are then detected in an electrical conductivity cell. The suppressor column and electrical conductibity detector distinguish ion chromatography from other types of ion exchange chromatography. In addition, ion chromatography requires ion exchange resin of unusually low capacity (~0.002-0.005 meg/ml).

These features give ion chromatography unique advantages for the analyses of common inorganic ions, especially anions. First, because the electrical conductivity detector is non-selective (responds well to any ionized species), several ions can be detected in a single analysis. Thus, unexpected and unanticipated ions may be detected. Second, detectability may be as low as a few ppb for common aqueous anions (Wetzel, 1979; Small, 1978), although this ability depends somewhat on the eluent. Third, methods for new analytes and matrices often can be developed by simply modifying flow rate, eluent composition, and column material. In contrast, the application of colorimetric or "wet chemical" methods requires the tedious development of new reactions for each species.

TABLE 3.5 CHROMATOGRAPHIC METHODS FOR INORGANIC IONS

Description	Reference
Introductory texts, including principles and numerous applications	Sawicki et al. (1978) Mulik & Sawicki (1979)
Dual ion chromatography using parallel columns patent	US Patent 3923460
Basic principles and instrumentation	Small et al. (1975)
Na^+, NH_4^+, K^+, Mg^+, Ca^+, Cl^-, NO_2^-, PO_4^{3-}, SO_4^{2-} in biological fluids	Courtney (1976)
SO_4^2 and NO_3^- in ambient aerosols	Mulik et al. (1977)
Paper chromatographic separation of S oxides	Steinle (1962)
AsO_2^-, AsO_3^-, F^-, Cl^-, NO_3^-, and SO_4^- in leachate	Steiber & Merrill (1979)
S and other acid-forming elements in fuels	Mizisin et al. (1979)
On-line ion chromatography for process control	Miller (1978)
Ion chromatography with coulometric detection for F^-, Br^-, Cl^-, I^-, CN^-, SCN^-, S^-, $S_2O_3^-$, and Fe(II) & Fe(III) cyanide complexes	Girard (1979)
As & S species in environment samples: also F^-, HCO_2^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, SO_3^{2-}, NO_3^-, SO_4^{2-}, AsO_4^{3-}	Hansen et al (1979)
Cl^-, SO_4^{2-}, PO_4^{3-}, and glycolate in boiler blowdown water	Stevens (1977)
Total Cl, Br, P, and S in organic compounds NH_3 and methylamines in water	Coluruotolo & Eddy (1977)
Common anions (Cl^-, PO_4^{3-}, NO_3^-, SO_4^{2-}) at ppb levels	Wetzel (1979)

TABLE 3.5 (continued)

Description	Reference
Column reactions of NO_2^-	Koch (1979)
F^-, Cl^-, NO_3^-, SO_4^{2-} in acidic pickling baths	Dulski (1979)
Thin layer chromatography for halides, CO_3^{2-}, IO_3^{2-}, NO_3^-, PO_4^{3-}, urea, citrate, and sulfur oxides	Mitchell & Waring (1978)
Dibutylphosphoric acid in nuclear fuel processing streams	Lash and Hill (1979)
Total S and Cl in organic compounds	Smith et al. (1977)
S species in oil shale wastewaters	McFadden & Garland (1979)
Paper and thin layer chromatography	Zweig & Sherma (1978)
Precision and accuracy with extracts from printed circuit boards	Wargotz (1978)
Time resolved molecular emissions	Al-Abachi et al. (1976)

As is any other technique, ion chromatography is subject to certain limitations. Obviously, the analyte must be ionized in water in order to be detected, must be inert during the separation, and must be separable from other ions dissolved in the sample. The eluent must be a form which can be neutralized in the suppressor column. Common eluents include NaOH, Na-phenate, $Na_2CO_3/NaHCO_3$, and Na_2-glutamate for the separation of anions, and HCl, $AgNO_3$, $Cu(NO_3)_2$, pyridine, and aniline for the separation of cations.

With these simple operating principles in mind, it is worthwhile to examine the experience of a few selected workers who have attempted to apply ion chromatography to complex samples. The reader is referred to Table 3.5 as well as the texts by Sawicki et al. (1978), and Mulik and Sawicki (1979) for a more comprehensive listing of applications.

McFadden and Garland (1979) studied the application of ion chromatography to the analyses of S species in retort waters. They successfully separated SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, and SCN^-. However, the oxides $S_2O_4^{2-}$, $S_2O_5^{2-}$, $S_2O_6^{2-}$, and $S_2O_7^{2-}$ were too unstable in solution, and no data could be developed. This fact raises the possibility that some of the S species in retort water undergo interconversions too rapidly to permit chromatographic separation. In their experience, McFadden and Garland could also easily separate F^-, Cl^-, NO_2^-, PO_4^{3-}, SO_3^{2-}, and SO_4^{2-} in retort water on a single column, and the ions I^-, $S_2O_3^{2}$, and SCN^- could be separated on a different column. Their eluent was 0.003 M $NaHCO_3$ + 0.002 M Na_2CO_3 for most separations.

Steinle (1962) attempted to separate the complex series of S oxides known as Wackenroder's solution using paper chromatography. He selected a 50:20:30:4:10 mixture of n-butanol, acetone, water, perchloric acid, and borium perchlorate as producing relatively little decomposition.

As with any chromatographic technique, on-column reactions are always possible, especially with particularly labile compounds. Such reactions are described by Schleffler (1979), who examined the stability of NO_2^- during ion chromatography. They observed that two peaks eluted even though the injected NO_2 was free of impurities, and that the relative intensities of the two peaks were related to the age of the suppressor column. They attributed this behavior to the formation of HNO_2 in the suppressor column, which was then separated by ion exclusion chromatography, and to the oxidation of NO_2^- to NO_3^- once the nitrite reached the acid front of the suppressor column.

Hansen et al. (1979) likewise report the decomposition of $SO_3^=$ during the ion chromatography. They found that the recovery of $SO_3^=$ depended on the total sample size, the retention time (eluent flow rate), and the presence of Fe(III) and Cu(II) (either in the same or in previous samples). Obviously, the determination of NO_2^- by ion chromatography needs be approached with caution.

Miller (1978) discusses the possibilities of using ion chromatography as on-line, real time analyzer for process control. The instrumental nature of ion chromatography is obviously better suited than are manual techniques for this approach.

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3.4 Dissolved Inorganics

3.4.1 Chloride

Because chlorine occurs in wastestreams as chloride (or chloride complexes), the determination of Cl^- also yields a reliable measure of total Cl. Unfortunately, the common colorimetric and titrimetric methods for Cl^- are poorly suited for retort waters without additional sample preparation. Each of these procedures depends for specificity on the reaction of Cl^- with Hg(II) or Ag(I) to form a complex or precipitate; in retort water many other species--such as $S^=$, $S_2O_3^=$, SCN^-, $SO_4^=$, and organic acids--are present in sufficient amounts to cause severe positive interferences. Fox et al. (1978) reported errors up to five fold using "wet chemical" methods for Cl in omega-9 retort water. Fox also reports the formation of a gelatinous precipitate during the titration of retort water with $Hg(NO_3)_2$, which obscures the endpoint.

Fortunately, these interferences can be removed by oxidation of the wastewater prior to analysis. For this purpose Haas (1979) employed H_2O_2, and Fox (1978) recommended boiling with HNO_3 followed by the addition of $KMnO_4$.

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3.4.2 Fluorine

Fluorine has traditionally been a difficult element to measure in complex samples for several reasons. First, instrumental methods, for which interferences are commonly minimized or at least understood, are only marginally useful for F, or can be applied only with unusual effort. This limits the analyst to "wet" methods.

Much of the interest in fluorine relates not directly to retort water but rather to leachates, vegetation, and solids. Almost without exception these materials are extracted or digested before analysis, and F is then measured in the aqueous form. The methods discussed in this section will therefore apply to digests and leachates as well as to retort water.

Table 3.6 contains a brief summary of the current literature treating the determination of F. By far the most common methods are the ion selective electrode and the colorimetric methods listed by the EPA (1979). The ion selective electrode is especially popular because of its wide dynamic range (0.1-1000 mg/l).

In 1978 Fox et al completed an interlaboratory analyses of F in retort water ("omega-9" water). Considering the complexity of the sample, the results were encouraging. At a F level of 60 mg/l the interlaboratory coefficient of variation was 16%, comparable to what is normally observed with ground and surface water (Staible, 1978). These results included seven laboratories using either the electrode or SPADNS method. These data therefore suggest that for omega-9 waters and other comparatively dilute retort waters, the ion selective electrode and SPADNS method are viable techniques.

Of course, not every waste stream or digest is as dilute as the omega-9 wastewaters, and other waste streams are more likely to contain additional interferences. Common interferences for the electrode include

TABLE 3.6. METHODS FOR F

Description	Reference
F ion selective electrode for biological materials: comparison with colorimetric methods	Roost & Sigs (1978)
Incorporation of ion selective electrodes into continuous flow systems	Cowell (1978)
The effects of Na, Ca, & Mg on the response of the F ion selective electrode	Smith et al. (1978)
AA spectrometry with background correction	Kinichi (1979)
AA spectrometry with a deuterium light source	Meglen and Kirkos (1979)
F in plants: sample preparation & handling	Cooke et al. (1976)
F in ores and slags: fusion in H_3BO_3/Na_2CO_3	Boniface & Jenkins (1977)
F in vegetation: an interlaboratory study	Jacobson & Heller (1978)
Standard methods: SPADNS colorimetric with distillation, ion selective electrode, and automated complexone	EPA (1979) APHA (1976)
Other colorimetric methods	Minin et al. (1976) Cupelin (1978)

Al, Cl, Fe, PO_4^{3-}, SO_4^{2-}, and hexametaphosphate. While these are not normally a problem and can often be masked, their significance increases in the analysis of brines and digests.

To separate such interferences, F is commonly distilled once or even twice prior to analysis. (EPA, 1979; APHA, 1978.) Forten (1977) and Meglen and Kriko (1979) have also described microdiffusion techniques in which the entire separation is completed inside a sealed beaker. The latter workers completed these steps by placing 10 ml aliquots of the sample in a 100 ml beaker. A 5 ml beaker containing 0.1 M Na_2CO_3 was then floated on the sample to serve as the F receptor. Heramethyldisiloxane was then added to the sample in order to form the volatile trimethyl fluorosilane (TMFS). The TMFS released F in the carbonate solution, completing a simple and inexpensive separation.

In this same study Meglen and Kriko also describe a molecular absorption technique, one of the few spectral techniques available for detecting F. Their approach is based on the absorption by AlF at 227.3 nm in a carbon rod furnace. Standard carbon rod atomic absorption instrumentation was used throughout, including a standard D_2 broadband lightsource. This technique was shown to be applicable in the range 0-3 mg/l with a standard deviation of approximately 5%. Above approximately 5 mg/l, the curvature of the working curve prevented accurate analyses. Numerous ions were seen to interfere in this approach, although these could normally be removed with the separation described in the previous paragraph.

Tsunoda (1979) also describes a graphite furnace atomic absorption technique for F utilizing the molecular absorption of AlF at 227.45 nm. Unlike Meglen, Tsunoda used a Pt hollow cathode line source (227.48 nm) to detect the AlF. This allowed him to use the D_2 continuum lamp to correct for background absorption and thereby to extend this technique to solutions containing up to 0.05 M NaCl. The dynamic range of this approach was approximately three to four times better (0-2 ng) than was achieved with a D_2 light source only (0-0.6 ng).

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3.4.3 Phosphorus

Fox et al. (1978) compared the results of total P and orthophosphate measurements which had been completed at several laboratories on the omega-9 wastewater. The values for total P varied by 83% relative, and the values for orthophosphate ranged from 0.08-24.6 mg/l. Clearly, not every method works equally well, and at the present time no single method can be selected a priori as the best. Fox's study included spark source mass spectroscopy, DC plasma optical emission, and two forms of the molybdenum blue colorimetric method (the first using stannous chloride as the reducing agent and the second using ascorbic acid).

While the stannous chloride molybdenum blue method for orthophosphate has been discontinued in most laboratories due to interference problems, the ascorbic acid/molybdenum blue method is still widely used and deserves further attention. This method is based on the formation of an Sb-P-Mo complex, which is then reduced by ascorbic acid to form a brightly colored dye. This procedure should therefore be subject to several classes of interferences, including other compounds capable of complexing Sb, P, or Mo, colored concomitants, any materials which are oxidized by the molybdate, and any materials which are more readily reduced than the Sb-P-Mo complex (EPA, 1979; Skougstad et al., 1979). While specific interfering compounds have not been identified in retort water, a number of possibilities obviously exist. Other interferences for this method include Ba, Pb, Ag, SiO_2, NO_2 and Fe.

Once a sample is thoroughly digested, the methods discussed in the previous paragraph should be more reliable. Nevertheless, the necessary digestion procedures have not yet been established for retort water, and this remains an area of needed research.

Other techniques capable of detecting total P at the levels anticipated in retort water include spark source mass spectroscopy, ICP spectroscopy, and DC plasma optical emission spectroscopy. These are covered elsewhere in this report and need not be discussed in greater detail here.

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3.4.4 Sulfur Compounds

Total Sulfur

For alternate measurements of total S by instrumental methods such as X-ray fluorescence, the reader is referred to Chapter 2 of this report. Section 3.3 also discusses ion chromatography as a technique for S speciation. In this section I discuss the more traditional methods for measuring total S and the various S species. Many such techniques require minimal equipment and are therefore more acceptable to the small laboratory.

At present the literature is highly contradictory regarding the viability of the standard methods for measuring total S. For example, Fox et al. (1978) completed an interlaboratory comparison using the omega-9 wastewater on which three laboratories attempted to determine total S through methods based on oxidation of the various S forms with H_2O_2 or Br_2. Results varied from 989 to 2700 mg/l. Wildeman and Hoeffner similarly found that the Br_2 and HNO_3 oxidation methods produced erratic results when applied to Paraho retort water. Leenheer et al. (in press) used the Br_2 oxidation method to determine total S in a series of in situ retort waters and achieved adequate reproducibility. They also analyzed for the S species SO_4^{2-}, SO_4^{2-}, $S_4O_6^{2-}$, and SCN^-, which accounted for 46 to 91% of the total S. Haas (1979) measured total S using the H_2O_2 oxidation of TOSCO II retort water. His results for total S also agreed well (86-~100% closure) with his results for S^{2-}.

Instrumental methods have been less than helpful in providing independent measurements of S. In Fox's study, for example, S was not detected by neutron activation, X-ray fluorescence, or any other instrumental technique. ($S \cong 2000$ mg/l). On the other hand, Fruchter et al. (1979) did detect total S in Paraho retort waters at levels of 3% using X-ray fluorescence and neutron activation. No comparisons of results were shown. Unfortunately, the detectability of neutron activation is marginal even at these levels, and X-ray fluorescence techniques suffer from significant self-absorption effects.

The determination of total S clearly deserves further attention. Fortunately, the literature describes many methods for measuring total S in addition to the methods described in this section. Table 3.7 summarizes several such methods, and the reader is referred there for an introduction to the literature. Several of the methods listed in Table 3.7 may be effective for retort water, although their value is yet to be thoroughly tested.

Sulfate

Table 3.7 references several of the common chemical methods of determining sulfate, including colorimetry, titrimetry, and gravimetry. The literature on methods for measuring sulfate is immense, and the reader is referred to Kolthoff and Elving (1961), Fishmann and Erdmann (1979), and Kuck (1978) for a concise review.

Although the various methods in Table 3.7 appear different at first glance, each relies on the precipitation (or complexation) of SO_4 with Ba. Rather than being fundamentally different, the variety of methods in this table represents efforts to improve ease of use, to match the working range to the sample, and to make use of readily available laboratory equipment.

Because each of these methods relies on the precipitation of $BaSO_4$ to distinguish SO_4^{2-}, interferences in one method tend to be common to all methods (Kothney et al, 1976). For example, sulfur compounds such as S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$ can readily form SO_4^{2-} or precipitate with Ba. Colored solutes and colloidal material interfere with the colorimetric methods for SO_4^{2-}. Efforts to avoid such interferences are described by Du Plessis and Hautman (1975), Lohka (1978), and Cronnan (1979). Other anions which are capable of precipitating with Ba (e.g. CO_3^{2-}, HCO_3^{2-},

TABLE 3.7. METHODS FOR S AND S-COMPOUNDS

Total S	References
Aqueous oxidation with Br_2	AOAC (1970)
Aqueous oxidation with H_2O_2	APHA (1955)
DC plasma/far UV spectrometry	Ellebracht et al. (1978)
X-ray fluorescence and other instrumental methods	See Chapter 2 of this report
Combustion and coulometric titration	Lange & Brumsack (1977) Wallace et al. (1970) White (1977)
General review of S methods, especially decomposition techniques	Kuck (1978) Kolthoff & Elving (1961) Meyer (1977)
S in in situ retort waters by Br_2 oxidation	Stuber et al. (in press)
S in Paraho retort water by NAA and vacuum XRF	Fruchter et al. (1977)
S in omega-9 retort water: interlaboratory comparison of H_2O_2 and Br_2 oxidation methods	Fox et al. (1978)
S in organic materials using the Perkin Elmer CHN analyzer	Culmo (1972)
S in various environmental samples with a flame photometric detector	Horton et al. (1971)
S in solids via high temperature combustion and titrimetric finish	Rice-Jones (1953) Mott & Wilkinson (1956)
Induction furnace combustion and titration	Craddock (1973)
Sulfate	
Standard Methods: Methylthymol blue, colorimetric Thorin, titrimetric Automated chloranilate, colorimetric Turbidimetric Gravimetric with Ba^{2+}	Skougstad et al. (1979) APHA (1976) EPA (1979) ASTM

TABLE 3.7 (continued)

Sulfate	References
General Reviews	Kolthoff & Elving (1961) Fishman & Erdmann (1979) Kuck (1978)
Evaluation of the methylthymol blue method	Bergman & Sharp (1976)
AA determination of precipitated $BaSO_4$	Campbell & Tioh (1978) Oeien (1979)
Ba-nitro sulfanazo-III dye colorimetric method	Hoffer et al. (1979) Pagenkopf et al. (1978)
Eliminating interference due to colored humic matter	Ogner & Haugen (1977)
Turbidimetric procedure	Verma et al. (1977)
Removal of interferences in colored samples	Du Plessis & Houtman (1975)
Potentiometric titration of colored liquors using an ion selective electrode	Lokka (1978)
Elimination of color interferences with H_2O_2 and UV irradiation	Cronan (1979)
Intermethod comparison	Kothny et al. (1976)
Interlaboratory comparison with omega-9 retort waters	Fox et al. (1978)
Analysis of various in situ retort waters	Stuber et al. (in press)
Thiocyanate, Thiosulfate and Other S Oxides	
$S_2O_3^{2-}$, $S_3O_6^{2-}$ by conversion to SCN	Kelly et al. (1969)
Colorimetric method for $S_2O_3^{2-}$ using Hg - chloranilate	Mehra & O'Brian (1976)
SO_3^{2-} by iodometric titration	EPA (1979)

TABLE 3.7 (continued)

Thiocyanate, Thiosulfate and Other S Oxides	References
SCN^- as ferric complex	APHA (1976)
Review of methods for SCN^-, $S_2O_3^{2-}$, $S_nO_6^{2-}$, and SO_3^{2-}	Kolthoff & Elving (1961)
Methods for SCN^- in retort water	Leenheer & Stuber (1979)
Automated dialysis to remove interferences in the Fe(III) method for SCN^-	Gosdon (1978)
SCN^- in blood selective oxidation to CN^- and distillation	Ballantyne (1977)
SCN^- in blood and urine; separation by ion exchange and determination as CN^-	Lundquist et al. (1979)
$S_2O_3^{2-}$, in urine/concentration by ion exchange	Sorbo & Ohman (1978)
Contribution of $S_2O_3^{2-}$ to BOD and COD in oil shale process water	Wang and Mercer (1979)
Sulfur oxides and SCN^- in various in situ retort waters	Stuber et al. (in press)
$S_2O_3^{2-}$, in Paraho retort water	Wildeman & Hoeffner (1979)
$S_2O_3^{2-}$, SCN^-, $S_4O_6^{2-}$, and SO_3^{2-} in omega-9 retort water	Fox et al. (1978)
$S_2O_3^{2-}$, in TOSCO II retort water	Haas (1979)
In TOSCO II retort water; sampling and determination with an ion selective electrode	Haas (1979)
Qualitative tests of various in situ wastewaters with Pb acetate paper	Stuber & Leenheer (1979)
Interlaboratory comparison with omega-9 retort water	Fox et al. (1978)
In Paraho retort waters using the methylene blue method	Prien et al. (1977)

TABLE 3.7 (continued)

Sulfide	References
by iodometric titration	Skougstad (1979)
Standard methods Iodometric titration Methylene blue method Removal of interferences	APHA (1976) EPA (1979)
Review of manual methods; removal of interferences	Kolthoff & Elving (1961)
Pulse polarography	Youssefi & Birke (1977)
Ethylene blue colorimetric method	Kirsten (1978)
With an ion selective electrode	Baumann (1974) McAnalley et al. (1979) Boczkowski (1977)
Review of current literature	Fishman & Erdmann (1979)
By fluorimetry	Vernon & Whitham (1972)

PO_4^{2-}, and SiO_4^{4-}) generate positive interferences. In the gravimetric procedures even soluble anions such as NO_3^- an ClO_4^- can co-precipitate, thereby yielding high results. Cations--such as Ba, Pb, Cr, Fe, and alkali metals also precipitate or co-precipate with $BaSO_4$ to yield high results. Agents which are capable of complexing Ba could also cause false values.

Considering the pitfalls in the "wet" methods for measuring SO_4^{2-}, the results with retort wastewaters have been suprisingly consistent. For example, Fox et al. (1978) analyzed the omega-9 wastewaters using the turbidimetric, gravimetric, and automated chloranilate methods. Results varied ± 13% relative, which is comparable to variations observed during the analysis of normal ground and surface waters (Staible, 1978). Leenheer (in press) also analyzed various in situ retort waters using the methylthymol blue method in duplicate and reported no exceptional difficulties. However, as discussed above, the basic principles behind these methods are the same, and their agreement does not imply accuracy.

Thiocyanate, Thiosulfate, and Other Sulfur Oxides

These species are discussed here as a group for two reasons. First, some methods for sulfur oxides selectively convert the various S oxides to SCN^-which then determined, so that discussions of one method naturally lead to discussions of others. Second, several workers are interested in S speciation in retort water and will therefore be interested in all the species in this group.

In this section I will first discuss the available analytical methods and then their application to retort water. This section deals mainly with the more traditional methods, colorimetry and titrimetry, while the newer chromatographic methods are included in Section 3.3. Due to space and time limitations, here I discuss only those methods which appear most relevant to oil shale wastewaters and refer the interested reader to Table 3.7 for a more complete review of the literature.

One of the more common methods for SCN^- relies on the reaction with Fe(III) to form the brightly colored ferric thiocyanate complex, which is then measured by optical absorption (APHA, 1976). This method can be easily automated (Leenheer, 1979), which accounts in part for its popularity. The APHA indicates the range for this method as 1-10 mg/l, using the manual method, although Leenheer and Stuber (1979) report a detection limit of 10 μg/l using the continuous flow technique.

The principal difficulty with this technique has been the number of interferences encountered in complex samples. These include agents capable of reducing Fe^{3+} to Fe^{2+}, materials which can complex with Fe^{3+}, and other colored solutes. Gosdan (1978) attempted to remove such interferences with continuous-flow dialyzer in which the SCN^- selectively diffused from the sample. Using this method Gosdon successfully analyzed plant extracts for SCN^-.

Leenheer and Stuber (1979) have optimized this technique for trace levels of SCN^- in waters containing unusually high levels of colored organic materials (including retort water). These workers successfully removed organic interferences with an XAD-8 resin, an innovation which allowed them to analyze in situ retort water as well as highly colored surface water from the Rio Negro. The interference due to phenol was also removed suggesting that this technique may be promising for waste waters from coal gasifiers as well. This entire procedure was completed on a Technicon autoanalyzer at a rate of 20 samples/hour.

The other major technique for trace levels of SCN^- is the Cu-pyridine method (Leenheer and Stuber, 1979). In comparison to the ferric-thiocyanate method, the Cu-pyridine method is supposedly less subject to interferences. However, it also requires extensive manual extractions and sample manipulation, and exhibits a poorer detection limit, considerations which led Leenheer to prefer the ferric-thiocyanate method.

Several workers have determined SCN^- indirectly after conversion to CN^- (Kolthoff and Elving, 1961; Ballantyne, 1977; Lundquist, 1979). For example, SCN^- can be reacted with chloramine-T to form CNCl, the usual intermediate to the determination of CN^-. Of course, these methods must respond to CN^- as well as SCN^-, so that specificity would be rather poor for samples as complex as retort waters. Neverthless, Ballantyne (1977) reports the application of this approach--after a distillation step--to whole blood, and Lundquist (1979) reports on a similar procedure for serum and urine. Lundquist also reports on the enrichment of SCN^- on ion exchange resin, an approach which should extend the range of any trace method for thiocyate and which may prove valuable for detecting SCN^- in retort water.

Many of the common methods for thiosulfate and the higher polythionates are best suited for simple solutions and not for retort waters. For example, the iodometric titration, which accurately measures thiosulfate in pure solutions, would lack adequate specificity and sensitivity for retort waters. (Kolthoff and Elving, 1961). The method described by Mehra and O'Brien (1976) relies on the reaction of $S_2O_3^{2-}$ with Hg-chloranilate to form HgS and soluble chloranilate. Unfortunately, any other species capable of reacting with Hg (such as S^2) would also yield a positive reading, a situation which clearly lacks the selectivity for the retort water.

$S_2O_3^{2-}$ is commonly determined simultaneously with the higher polythionates $S_3O_6^{2-}$ and $S_4O_6^{2-}$ through the selective cyanolysis of polythionates according to the reactions (Kelly et al., 1969):

$$S_4O_6^{2-} + 3CN^- + H_2O = S_2O_3^{2-} + SO_4^{2} + 2HCN + SCN^- \qquad (3.1)$$

(3.2) $$S_2O_4^{2-} + CN^- \underset{\text{catalyst}}{\overset{Cu^{2+}}{=}} SO_3^{2-} + SCN^-$$

(3.3) $$S_3O_6^{2-} + 3CN^- + H_2O = SO_3^{2-} + SO_4^{2-} + 2HCN + SCN^-$$

The first reaction occurs readily at 5°C, the second requires a Cu^{2+} catalyst, and the third takes place only near boiling. When the reactions are complete, SCN^- is determined as the ferric complex, as discussed above. The particular advantage to this technique is its detectability, which is adequate for most retort waters.

Kelly originally developed this technique using solutions containing $S_2O_3^{2-}$ and polythionates only. He also reports adequate results with bacterial culture media. However, extension of this technique to retort water appears somewhat premature pending a more rigorous investigation. For example, does retort water contain indigenous catalysts for reactions 3.2 or 3.3?

Another disadvantage of this method is that concentrations are related to differences in absorbance in a series of samples, rather than to absolute absorbance. For example, in order to complete reaction 3.3, reactions 3.2 and 3.1 also occur and contribute to the total SCN^-.

Table 3.7 references several articles that describe the analysis of retort water for SCN^-, $S_2O_3^{2-}$, and polythionates. In general, these investigators have used the cyanolysis and ferric thyocyanate method and do not report any unusual difficulties. However, these results must be weighed in view of the paucity of comparative techniques.

Sulfite

Sulfite has not been widely measured in retort waters, perhaps because of the lack of adequate techniques. For example, the standard method recommended by the APHA (1976) is designed more for boiler feed water than complex wastewaters. This procedure is based on the oxidative titration with a iodide/iodate solution. Other oxidizable species such as $S_2O_3^{2-}$, S^{2-}, some organic matter, and perhaps even NH_3 would thus be expected to interfere. Other common methods for SO_3^{2-} are also subject to many interferences (Kolthoff and Elving, 1961). Thus, Fox (1978), in her interlaboratory comparison of analytical methods, was able to measure SO_3^{2} using only one technique (IO_3^- titration), and these results were expected to be in error by more than 50 fold.

Sulfide

In surface and ground waters sulfide is commonly determined by the methylene blue colorimetric method or by an iodometric titration. Both methods exhibit more than sufficient detectability (~ 1 mg/l) for retort waters; both methods are also subject to several interferences which may proscribe their application to certain retort waters (EPA, 1979; APHA, 1976; Skougstad, 1979).

The iodometric method responds to any reducing agent which reacts with iodine, including the various sulfur oxides which are found in some retort waters. Other possible interferences in retort water would include ammonia and unsaturated organic compounds. The methylene blue method is subject to similar interferences, as discussed in more detail in Chapter 4 of this report under the topic of H_2S measurements.

Because of these interferences, methods have been developed for separating sulfide from the rest of the sample. For example, Kolthoff and Elving (1961) recommend acidifying the sample and purging the resulting H_2S into a bubbler containing zinc acetate. The resulting ZnS precipitate can then be analyzed by either common method. Similarly, the APHA (1976) recommends separating sulfide by adding zinc acetate and removing the ZnS precipitate. Either method is most likely to succeed when sulfide is the only form of S present. However, for waters containing a mixture of reduced S compounds--such as some retort water--the removal of sulfide may upset the equilibrium and produce additional H_2S. In any case, either separation technique should yield values which represent at the very least an upper limit to the sulfide concentration.

Several others have reported on the application of the AgS ion selective electrode for the determination of sulfide. (Boczkowski, 1977; Baumann, 1974; McAnalley et al., 1979). A typical approach is to titrate sulfide with soluble lead while measuring the cell potential. This method is not only convenient, but it should also be free of interferences due to reducing compounds (in contrast to the iodometric and methylene blue methods). However, the response of this technique to other S compounds which may convert to sulfide upon the precipitation of the PbS remains an open question.

Polarography, fluorimetry, stripping voltammetry and other types of colorimetric methods have also been applied to the determination of sulfide (Table 3.6). Advantages of these techniques for the analysis of retort waters are not readily apparent at this time.

The literature to date has been inconclusive regarding the application of the techniques discussed in this section to retort waters. For example, Fox et al. (1978) measured the concentration of sulfide using two techniques: (1) acidification and purging to separate the sulfide followed by the iodometric titration, and (2) the qualitative lead acetate test. The two iodometric results were erratic (116-176 mg/l), and the lead acetate method did not detect sulfide, a result which was taken to imply that the sulfide concentration was < 20 mg/l. Fox argued that the acidification step in the first procedure decomposed other reduced S compounds, and that reduced organic compounds were carried over during the purging step. Either possibility would cause high and possibly erratic results. On the other hand, the detection limit of qualitative tests, such as the lead acetate paper method, should not be interpreted too strictly. In summary, Fox's data does not establish a test method for sulfide in retort water, and some doubt is cast on the acidification/purging process.

Haas (1979) determined sulfide in TOSCO II retort water with a AgS ion selective electrode. He reported no operational problems such as drifting or erratic results. In addition, his results showed excellent agreement with parallel measurements of total S. This result is reasonable for an indirect retorting process where sulfide is the major dissolved sulfur species (Section 3.0). Similarily, Prien et al. (1977) measured sulfide in Paraho retort water and reported no operational problems. However, neither Haas or Prien employed more than one technique so intermethod comparisons are not possible.

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3.4.5 Nitrogen Compounds

Cyanide

Table 3.8 references several techniques for the measurement of CN^- along with two applications to the analysis of retort water. The most commonly practiced techniques include the pyridine-barbituric acid colorimetric method, the $AgNO_3$ titrimetric method, and the ion selective electrode method, each of which have more than adequate detectability (0.02, 1.0, and 0.05 mg/l respectively) for the analyses of retort water. Unfortunately, all of these techniques are subject to interferences which may proscribe their application to retort water. Interference compounds which are found in retort water include sulfide, thiocyanate, fatty acids, and some organic nitrogen compounds (Skougstad, 1979; APHA, 1976; EPA, 1979).

Such interferences are often separated by an acid distillation which precedes the analysis. In addition, sulfides can be precipitated by the addition of $CdCO_3$, and fatty acids can be removed by extraction with an organic solvent. However, such separations are never 100% efficient and can even cause additional problems. For example, during the acid distillation SCN^- and organic nitrogen compounds may decompose to yield CN^-, thereby leading to incorrectly high results. Whether such reactions occur during the analysis of retort water remains to be answered.

In her interlaboratory comparisons of analytical methods, Fox (1978) determined CN^- in omega wastewater by the manual pyridine-pyrazolone method and by the automated (Technicon) digestion/pyridine-barbituric acid method. A total of three analyses were reported with values ranging from 0.42 to 2.9 mg/l, suggesting a problem with at least one of the techniques.

TABLE 3.8 METHODS FOR NITROGEN CONTAINING COMPOUNDS

Cyanide	References
Standard methods: Distillation followed by	EPA (1979)
Pyridine-pyrazolone colorimetric procedure	APHA (1970)
Pyridine-barbituric acid colorimetric procedure	Skougstad (1979)
Titration with $AgNO_3$	ASTM (D2036)
Ion selective electrode	
Ion selective electrode	Frank et al. (1972)
Reviews	Fishman & Erdmann (1979)
By gas chromatography	Nota et al. (1977)
In biological fluids by fluorescence	Morgan et al. (1976)
Removal of interferences with ion exchange columns	Nakahara (1976)
Distillational and potentiometric determination in biological materials	Egekeze & Oehme (1979)
Interlaboratory comparison with omega-9 wastewater	Fox et al. (1978)
In TOSCO II retort water using ion selective electrodes	Haas (1979)
Total Ammonia And Ammonium	
See Chapter 5	
Total Nitrogen	
General Reviews	
Microchemical organic analyses	Tolg (1970)
Kjeldahl and Dumas method	Fleck (1974)
Combustion reactions	Ebel (1973)

TABLE 3.8 (continued)

Kjeldahl method	
Standard protocols	EPA (1979) APHA (1976) Skougstad (1979)
Review of recent modifications	Fishman & Erdmann (1979)
Unattended, micro distillation	O'Deen & Porter (1979)
Of plant material containing NO_3^-	Eastin (1978)
Addition of H_2O_2 for the analysis of organic material	Dardasz & Roszyk (1978)
Review of Kjeldahl and Dumas methods	Fleck (1974)
Applications	
Omega-9 wastewater by Kjeldahl procedure	Fox et al. (1978)
Organic bases by column chromatography in situ retort waters	Stuber & Leenheer (1977)
Paraho retort water by Kjeldahl procedure	Prien et al. (1977)
Procedures based on hydrogenation	
Trace levels in petroleum products	Holowchak et al. (1952)
Petroleum products, with automated coulometric titration	Martin (1966) ASTM D 3431-75 Oita (1971)
Ammonia and total N in municipal wastewater with automated coulometric titration	Albert (1969) Faffro et al. (1971)
Various environmental samples for total N and isotope ratio: electrolytic conductivity and mass spectrometer detectors	Carter et al. (1975)
Petroleum to 0.1 ppm N	Rhodes et al. (1971)

TABLE 3.8 (continued)

Procedures based on combustion	
Automated CHN analyzer with thermal conductivity detectors	Condon (1966)
Simultaneous determination of C,H,N, S,F,Cl,Br, and I with a mass spectrometer detector	van Leuven (1973)
Isotope ratios and total N with a mass spectrometer	Tsuji et al. (1975)
N and C in water with a GC finish	Miyagi (1976)
Freeze-dried seawater samples with an automated CHN analyzer	Sharp (1973)
Petroleum fractions, with a chemiluminescence NO detector	Drushel (1977)
Sealed tube combustion; detection with pressure gage following fractional distillation of combustion products	Stump & Frazer (1973)
C,H,N,S, and O with a GC finish	Dugan & Aluise (1969)
Sealed tube combustion with Cu/CuO	Heck & Jones (1963)
Nitrate	
Review of available techniques: colorimetry, ion selective electrodes, voltammetry, polarography, gas chromatography, titrimetry, gravimetry, and automation	Fishmann & Erdmann (1979) Clear & Roth (1961)
Standard Protocols Brucine colorimetric Cd and hydrazine reduction methods Ion selective electrode Chromatotrophic acid colorimetric Direct UV absorption Devardas alloy reduction method	EPA (1979) Skougstad et al. (1979) Nrisinha & Donaldson (1978) APHA (1976)

TABLE 3.8 (continued)

In omega-9 wastewater	Fox et al. (1978)
In Paraho retort water	Prien et al. (1977)
Ion selective electrodes	
By gas chromatography, after conversion to nitrobenzene or other aromatic derivatives	Ross et al. (1975) Tanner et al. (1979) Tesch et al. (1976) Toyoda et al. (1978)
Enzymatic reduction to NO_2^-	Senn et al. (1976)
Design of an ion selective electrode; selection of solvent	Hulanicki (1978)
Soil extracts, by automated ion selective electrode	Hansen et al. (1977) Simeonov et al. (1977) Forney & McCoy (1975)
Effect of Cl on Cd and hydrazine reduction methods	Hildrum (1979)
In fertilizers, by ion selective electrode	Barbera (1977)
Brucine method for saline and fresh waters	Jenkins & Medsker (1964)
By reduction to NH_4^+	Bochkarev (1978)
In milk and tobacco: diphenylamine method	Mrowetz (1977) Harvey (1979)
Comparison of methods	Mueller & Stepe (1979)

Total Nitrogen

Most methods for measuring total nitrogen begin by converting all forms of nitrogen to a common species according to one of the following procedures:

- aqueous digestion in H_2SO_4 to form dissolved NH_4^+ (Kjeldahl method)
- combustion to N_2 or NO (Dumas or Pregel-Dumas methods)
- hydrogenation to gaseous NH_3 (ter Muelen method)

A wide variety of techniques ranging from manual gas absorption trains to mass spectrometers and automated coulometric titrators, can be used to quantitate the nitrogenous reaction product. Table 3.8 summarizes current literature on each of these approaches for the reader desiring in-depth descriptions of the various detection schemes.

Of the techniques discussed in the previous paragraph, the Kjeldahl method is widely used for surface and wastewaters, while the other techniques are more common for oils, solids, and synthetic organic chemicals. However, there is reason to suspect that the Kjeldahl technique is not suited for retort water because of its inability to respond to several classes of nitrogenous organic compounds, including hydrazones, oximes, nitro-compounds, semi-carbazones, azides, nitriles, and azo-compounds. Unfortunately, organic bases are a major component of retort water, accounting for up to 25% of the dissolved organic carbon (Leenheer, 1978; Prien, 1977). The Kjeldahl method may also miss nitrate, depending on the exact modification employed (Fishmann and Erdmann, 1979; Eastin, 1978; Fleck, 1974). Because of these difficulties, the result of the

Kjeldahl procedure is normally referred to as "total Kjeldahl nitrogen" rather than as "total nitrogen".

Fox et al. (1978) analyzed omega-9 wastewater using both automated and manual versions of the Kjeldahl procedure. Their results were within ± 12% (1 σ, n=4), suggesting this technique to be adequately precise. Accuracy was not established because of the problems mentioned in the previous paragraph and because the Kjeldahl procedure was not compared to other techniques. Prien et al. (1977) also measured total Kjeldahl nitrogen in Paraho retort water and reported no operational problems.

The hydrogenation (ter Muelen) procedures for total nitrogen appear attractive as an alternate method for several reasons. First, the ter Muelen procedure more readily detects refractory organic N compounds than the Kjeldahl procedure. The ter Muelen procedure also responds to inorganic and oxidized forms of N, such as NO_3^-. Second, detectability is more than sufficient for retort waters, being in the sub-ppm range (∿ 1 ng). Third, automated systems are commercially available which determine the NH_3 produced, typically by coulometric titration. A complete analysis can supposedly be obtained with such systems in approximately 10 minutes, a substantial improvement over the manual Kjeldahl procedure.

In addition to coulometric titration many other schemes are available for determining the ammonia product. (See Table 3.8.) For example, Carter et al. (1975) used a Coulson electrolytic conductivity GC detector to quantitate the NH_3 and a mass spectrometer to measure the N isotope ratios. Colorimetric and titrimetric finishes have also been reported, especially in the older literature (Tolg, 1970).

Although the ter Muelen procedure has been widely applied to petroleum products, several authors also report on its application to water (Table 3.8). Rhodes and Hopkins (1971) point out that the formation of CO_2 during the hydrolyses of water or other oxygenated substances can lead to negative interferences when NH_3 is determined coulometrically.

They solved this problem with an Ascarite trap upstream from the titration cell. Albert et al. (1969) solved the same problem by humidifying the H_2 stream and using a CaO scrubber in place of the Ascarite trap. Albert analyzed municipal wastewater with the ter Muelen/coulometric system as well as by the Kjeldahl procedure. Excellent agreement was seen except for samples containing NO_3^-, in which case the Kjeldahl procedure gave low results. Accuracy and precision were approximately ± 6%. Fabbro et al. (1971) discuss in detail the instrumental requirements needed to measure N in wastewater, including furnace temperature, scrubber composition, and catalyst behavior. Samples of raw sewage and organic and inorganic salts in water were analyzed and gave excellent agreement with the expected values.

Combustion techniques have been largely limited to organic solids and liquids containing N in the percent range. For example, of those methods cited in Table 3.8, only those using mass spectrometry or chemiluminescence are likely to be sensitive enough for measuring N in retort water. Since few laboratories would be willing to devote a mass spectrometer to analyze N, this leaves the chemiluminescence detector as the main contender. In addition, as most combustion techniques have been designed primarily for organic materials, it is difficult to predict how effectively they would operate with a water sample. In summary, it is not clear at this time whether combustion techniques could be useful for determining total N in retort water.

Total Ammonia and Ammonium

Before starting this section a word is in order regarding terminology. In this discussion the term ammonia refers to dissolved, unionized NH_3, written as $NH_3 \cdot H_2O$; ammonium refers to the ion NH_4^+; total ammonia, written as t-NH_3, refers to the sum of the latter two species, t-$NH_3 = NH_3 \cdot H_2O + NH_4^+$. Most methods measure t-NH_3, leaving the analyst with the problem of distributing this value between the two possible forms.

$t\text{-}NH_3$ is typically one of the major species in retort water and as such has been determined frequently. Common methods include (1) direct measurement by ion selective electrode, (2) distillation from a basic medium followed by titration with H_2SO_4, and (3) automated colorimetric procedures (Skougstad, 1979; EPA, 1979; APHA, 1976). For example, Wildeman and Hoeffner (1979) and Prien et al. (1977) both determined $t\text{-}NH_3$ in Paraho wastewaters using method 2. Haas (1979) employed method (1) for the anaysis of TOSCO II retort water. Wildeman's data suggested that $t\text{-}NH_3$ measurements were reproducible within approximately ± 10%. The other investigators reported no operational problems such as irreproducible results or drifting electrode potentials.

Fox et al. (1978) compared three methods for the analysis of omega-9 wastewaters: (1) basic distillation into H_3BO_3 followed by titration with H_2SO_4, (2) basic distillation into H_3BO_3 followed by the automated phenolate finish, and (3) direct measurement by ion selective electrode with no distillation. A total of 5 analyses yielded an average of 3800 mg/l ± 10% RSD. This data suggests that any of these methods are adequate for retort water. Thus the selection of a technique could be based primarily on ease of application and availability of equipment.

Because $t\text{-}NH_3$ in retort water readily evolves upon addition of base, several opportunities occur for combining the measurements of total nitrogen (t-N) and $t\text{-}NH_3$. For example, if t-N is measured by combustion to NO followed by chemiluminescence detection, $t\text{-}NH_3$, should be measurable by purging from a basic solution into the same combustion train. Similar opportunities occur for most of the techniques discussed under "Total Nitrogen". Albert et al. (1969) developed such an apparatus based on the hydrogenation of N compounds followed by a coulometric titration for NH_3: $t\text{-}NH_3$ is determined with the same system by purging from base into the system following the hydrogenation furnace.

Somewhat more difficult than measuring $t\text{-}NH_3$ is estimating its distribution between $NH_3 \cdot H_2O$ and NH_4^+. In dilute surface waters this distribution can be calculated by using the equilibrium constant for the reaction

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^-$$

However, as pointed out in Section 3.1, such equilibrium constants are not necessarily applicable to the brines produced by oil shale retorting.

The position of this equilibrium is important for two reasons. First, knowledge of the NH_4^+ concentration is essential to calculate the charge balance, and therefore serves a quality assurance function. Second, wastewater "strippers", which may be used for treating retort water, respond to the vapor pressure of gaseous NH_3, which is proportional to $NH_3 \cdot H_2O$. Fortunately, the latter can be measured directly, at least at room temperature, with an ammonia ion selective electrode operated without the normal addition of base.

Nitrate

Nitrate has not been widely measured in retort water, perhaps because the available analyses (Fox et al.,1978; Prien et al.,1977) indicate it to be a minor component (0.17 to 118 mg/l). However, its measurement may be important in regulating and monitoring biological digestion processes.

Fox et al. (1978) reported only one measurement (brucine method) of NO_3^- in their interlaboratory comparison of omega-9 wastewater. Prien et al. (1977) also employed the brucine method for the analysis of Paraho retort water. Neither group reported any obvious operational problems, but no data is available on the precision and accuracy of this method as applied to retort water.

Table 3.8 lists a number of methods for NO_3^-. The determination of NO_3^- has been reviewed extensively and need not be repeated here. (Table 3.8.) However, Table 3.9 lists characteristics of the more common methods which may be pertinent to retort water analysis. Clearly, each of the common methods has interferences which may be significant in retort water, and no method can be recommended without additional, empirical testing.

TABLE 3.9. CHARACTERISTICS OF COMMON METHODS FOR NITRATE

(Many of the interferences can be avoided by sample pretreatment)

Method	Range (mg/l)	Interferences
Brucine	0.1-50	strong oxidizing agents NO_2 organic matter Fe, Mn
Cd reduction (automated or manual)	0.01-1.0	suspended matter Fe, Cu, oil and grease colored organic material
Automated Hydrazine reduction	0.01-10	S^2 S colored organic material
Chromatotrophic acid	0.1-5	Cl_2, some oxidants NO_2, Ba, Pb, Sr, I, Se, colored organic matter
Direct UV absorption	0.04-10	colored organic material NO_2 Cr, Surfactants
Ion selective electrode	0.2-1400	Cl^-, HCO_3^-, NO_2^-, S^2

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4.0 GASES

As with any other sample, knowing the major components of a gas stream is helpful in selecting and developing analytical methods. The composition of retort gas depends on the type of retorting process as well as on the original shale. Two major categories of retort gases are recognized: high heat-content gases and low heat-content gases. The latter are produced by processes which introduce air directly into the retort ("direct processes"), while the former are produced by retorts which exclude air from the retort ("indirect processes").

Typical analyses of both types of gases are given in Table 4.1. As can be seen, the direct process gas is generally more dilute because of the presence of N_2. In addition, the gas composition is also affected by retorting temperature and by whether or not steam is injected into the retort. For example, NH_3 and CO_2 formation are both enhanced by higher temperatures. To complicate matters further, the gas undergoes a series of cooling and scrubbing processes, and the analyst must be prepared to deal with each of these modified gas streams. For example, gas from the TOSCO retort may pass through a fractionator to remove the shale oil vapors and NH_3, a compressor, a cooler for removing water vapor, scrubbers for removing the lighter hydrocarbons, and a sulfur removal unit. Gas analyses may be required at any point in this treatment train.

Although Table 4.1 shows the major components, equally important are several species which are not shown. Water will be present at all stages, typically as a saturated vapor at temperatures ranging from 30-100°C. Other forms of S besides H_2S, such as SO_2, COS, CS_2, and mercaptans, may escape removal by S control equipment which is designed specifically for H_2S. HCN and NO_x poison the action of some sulfur

TABLE 4.1. TYPICAL COMPOSITION OF RETORT GASES[a]

	Direct Process Gas	Indirect Process Gas
H_2	4.30	24.8
O_2	0.87	~0
N_2 + Ar	63.70	0.7
CH_4	2.20	28.7
CO	2.00	2.6
CO_2	21.80	15.1
H_2S	0.30	3.5
NH_3	0.71	1.2
C_2H_4	0.92	9.0
C_2H_6	0.95	6.9
C_3H_6	0.45	5.5
C_3H_8	0.47	
C_4 hydrocarbons	0.40	2
C_5 hydrocarbons	0.16	
C_6+ hydrocarbons	0.77	
Total	100.0	100.0
Heat content (Btu/scf)	100	900

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[a] All results are in volume %, dry basis (Neven et al., 1979).

removal devices (such as Stretford units). Tars and heavier hydrocarbons may condense in sulfur control units, thereby destroying expensive scrubbing liquors. Volatile trace elements such as Hg must be measured in the retort gas so that their fate in the retorting plant can be known.

Most gases shown in Table 4.1 should be stable during their transit through the plant. However, upon exposure to liquid water, a wide variety of reactions is possible, such as those described in Section 3.1 of this report. These include the reaction of SO_2 with H_2S to form Wackenroder's solution, and the reaction of HCN, SO_2, and H_2S to form SCN^-. These reactions are important because many sampling trains cool the gas sample in order to remove excess water, thereby exposing the sample to liquid water. Soluble gases such as NH_3, CO_2, and SO_2 would be dissolved in this condensate and thus never reach the gas analyzer. Clearly, the use of gas coolers and driers to pre-treat the gas stream must be approached cautiously.

For several of the species discussed in the last paragraph, especially regulated pollutants, standard analytical methods as well as commercially available instruments have been developed for either ambient air or thoroughly combusted stack gases. A very few methods and instruments have also been developed for the determination of such species in natural gas. In comparison, retort gas represents a significantly more complex mixture, and it cannot be safely assumed that existing techniques can be extended without modification to retort gases.

In the sections that follow, I discuss the experience of various researchers who have sampled and analyzed retort gases. However, it is common in the literature to find retort gas analyses with only brief and often inadequate descriptions of methodology. Principally lacking are tests for interferences and descriptions of reproducibility and reliability.

For these reasons I have prepared an annotated bibliography listing not only applications in oil shale, but also related studies (Table 4.2). The first section in Table 4.2 provides general references on the sampling and analysis of gas mixtures as well as on methods of preparing standards. The texts in this section are recommended as primers for anyone first attempting gas analysis.

The following sections deal primarily with the analysis of sulfur and nitrogen contaminants in retort gases. Since development plans for oil shale plants include the combustion of retort gas, N and S compounds would provide precursors for SO_2 and NO_x emissions unless controlled. The determination of these compounds should therefore play a major role in operating and evaluating control equipment, which may be placed prior to the gas combustion stage.

Once the gas is combusted, it will closely resemble the stack gases common to utilities and industrial boilers, and should not produce any unusual analytical problems. I therefore assume that standard methods and commercial analyzers will be appropriate for combusted gas streams, and do not plan further discussions here.

TABLE 4.2. REFERENCES FOR THE ANALYSIS OF RETORT GAS

GENERAL REFERENCES: Reviews, Compendia, and Summary Documents

Sampling, analysis, standardization, and a compendium of detailed protocols	APHA (1977)
Practical advice on stack sampling, especially with EPA-approved methods	Benchley (1974)
Instrumental techniques	Barras (1974)
Commercially-available instruments for ambient and source monitoring	LBL (1976)
EPA-approved methods for source monitoring new source performance standards	PEDCO (1977)
Preparation of standard gases	Nelson (1971)
Sampling, analysis, standardization, and a compendium of detailed protocols	Leithe (1972)
New instrumental techniques	Stevens and Harget (1974)
Accuracy and precision	APCA (1976)
A compendium of analytical methods for monitoring the industrial environment	AIHA
An extensive list of methods for monitoring the industrial workplace	NIOSH (1979)
Gas monitoring in the oil shale industry: anticipated regulations	Oil Shale Work Group (1979)

TOTAL S and REACTIVE N

Reductive hydrogeneration of S compounds	Cedergren & Luden (1977)
Total S in organic compounds	Beuerman & Meloan (1962)
N,S,P, and C in biological materials S in petroleum	Horton et al. (1973)

TABLE 4.2 (continued)

TOTAL S and REACTIVE N	
Comparison of oxidative and reductive methods	Wallace (1970)
Automated coulometric titration for S	Glass & Moore (1980)
Total S with a FPD detector	APHA (1977)
Total S by combustion/acid-base titration	ASTM D 1072
Total S by hydrogeneration	ASTM D 3031
APPLICATIONS	
AsH_3, HCN, NH_3, CS_2, COS, H_2S, SO_2, SO_3, NO_2, and organics in Paraho retort gas	Prien et al. (1977)
Sulfur gases and trace metals (Hg and As) in Paraho retort gas	Freichter et al. (1979)
Major gases, H_2S, SO_2, hydrocarbons C_1- C_6, CO : A review for various retorts	Nevens et al. (1979)
Standard EPA methods applied to in situ retorting CO_2, N_2, O_2, orsat particles, SO_2, NO_x, SO_3, H_2S, NH_3, & HCN	Owen & McDonald (1979)
USBM retort: GC determination of CO_2, O_2, N_2, CH_4, CO, & H_2	Beck et al. (undated)
Hg in retort gas	Fox et al. (1978) Girwin et al. (1979
Review of previous studies	Sheesley (in press)
Gases from the Fisher assay	Goodfellow & Atwood (1974)
OTHER SPECIES	
CS_2 in the workplace by collection in copper acetate/ethanol solution	Leithe (1970)

TABLE 4.2 (continued)

TOTAL S and REACTIVE N	
As species by selective sorption	Johnson & Braman (1975)
CS_2 in the workplace	NIOSH (1979)
Major gases by GC	Smith (1975)

4.1 Hydrogen Sulfide

This section discusses methods which detect only H_2S, while chromatography, microwave spectroscopy, and other multi-species techniques are discussed elsewhere in this chapter. For the interested reader, Table 4.3 provides a summary of recent literature on the measurement of H_2S.

4.1.1 Manual Methods

Most manual (i.e. "wet chemical") methods for H_2S are based on the collection of sulfide as a stable precipitate, followed by an analysis for sulfide. One example is the EPA Method 11, which is designated for compliance monitoring of point sources. In this method the sample stream is bubbled through a suspension of $Cd(OH)_2$ and is thereby collected as CdS. The CdS is dissolved and the sulfide is measured with an iodometric titration (PEDCO, 1977).

The standard methods recommended by other quasi-official agencies are similar. For the determination of H_2S in air the APHA (1977) recommends the collection in $Cd(OH)_2$ suspension followed by the measurement of sulfide using the methylene blue method. The AIHA (undated) describes methods for industrial atmospheres which are based on the collection of $CdCl_2$ or $CdSO_4$ solutions in place of the $Cd(OH)_2$ suspension, again followed by an iodometric titration. For the determination of H_2S in natural gas up to levels of 23 mg/l, the ASTM recommends collection in zinc acetate solution followed by the methylene blue method (Method D-2725). An alternate ASTM method (D-2385) provides for collecting the H_2S in $CdSO_4$ solution, followed by an iodometric titration.

An alternate method for the industrial atmosphere described by the AIHA is unusual in that it does not collect a sulfide precipitate. Instead, the sample is bubbled through a solution of I_3^-. The concentration of H_2S is given by the time required to decolor the solution.

TABLE 4.3. METHODS SPECIFICALLY FOR HYDROGEN SULFIDE

Summary of commercial H_2S and SO_2 monitors	LBL (1976)
H_2S in the atmosphere by collection $Cd(OH)_2$	APHA (1977)
H_2S in the atmosphere: survey of methods	Leithe (1971)
H_2S in the workplace: collection in I_3^-, $CdCl_2$, and NaOH solutions	AIHA (undated)
H_2S in point sources. EPA method 11	PEDCO (1977)
Electrochemical generation of standard gases: mercurimetric determination	Walendziak (1977)
H_2S in the atmosphere with fluorescent dyes	Tanaka (1977)
H_2S in the atmosphere by direct atomic absorption spectroscopy	Kovatsis (1976)
H_2S by colorimetry	Smirnova (1976)
H_2S in the atmosphere by ion selective electrodes	Hegyessy (1978)
H_2S in the workplace: comparison of instruments	Bostrom (1978)
Electrochemical cell for H_2S	Peterson (1978)
Detection by changes in conductivicity of a semiconductor	Wolff (1976)
Chemical sorbents to remove NO_2, O_3, $COCl_2$ interferences	Kroneisen (1975)
H_2S in natural gas: collection in $CdSO_4$ or $Zn(CH_3CO_2)_2$	ASTM D 2725 ASTM D 2385
H_2S by absorption in $Cd(OH)_2$ suspension & methylene blue finish	Adams (1975)
H_2S & total S in natural gas by coulometric titration	Austin (1977)
Performance characteristics of a polarographic H_2S analyzer	Sedlak et al. (1976)

Because these methods were not designed for retort gases, their effectiveness in this situation is unclear. However, several potential problems exist. First, any other S-containing gas which forms a sulfide precipitate with Cd will cause a positive interference. For this reason EPA Method 11 requires an impinger containing H_2O_2 upstream from the $Cd(OH)_2$ impinger in order to remove any SO_2. Under normal circumstances the H_2O_2 impinger supposedly passes H_2S. However, retort gas often contains levels of NH_3 which should make the H_2O_2 solution basic and thereby a potential collector for H_2S.

In addition, the fate of other sulfur gases such as COS, CS_2, and mercaptans in the EPA sampling train is not clear. However, since their levels in retort gas are probably slight compared to H_2S, it is unlikely that they represent significant interferences under normal plant operation.

The presence of the H_2O_2 impinger also provides a possible site for Wackenroder's reaction to take place. (See section 3.1.) This reaction would remove both SO_2 and H_2S.

Once H_2S is collected as a sulfide, several problems remain in the analysis. The iodometric titration depends on the reaction

$$H_2S + I_2 \rightarrow S + 2H^+ + 2I^-$$

However, under basic conditions part of the sulfide is also oxidized to sulfate, while under acidic conditions, some of the sulfide may be lost as H_2S (Kolthoff & Elving, 1961). Of course, any reducing agent which can be oxidized by I_2 is potentially a positive interference in retort gas. The effect of NH_3 and olefins on the determination of H_2S is therefore subject to question.

The methylene blue colorimetric finish also includes potential interferences. This method relies on the reaction of sulfide with N,Ndimethyl-p-phenylenediamine to form methylene blue. Reducing agents generally inhibit color formation, although this effect can be masked by adding extra Fe(III). Unless they are properly compensated for, species in retort gas such as SO_2, NH_3, CO, and olefins may represent negative interferences. In addition, it should be recalled that reducing agents such as $S_2O_3^=$ and SCN^- are formed in the condensate from retort gas (Section 3.1). One must ask then whether similar products are formed as retort gas passes through the cooled impinger solutions. In the methylene blue method NO_x is also a negative interference if present during sample collection (APHA, 1977)

In addition to such interferences, other problems with the manual methods have been described (APHA, 1977):

- sensitivity to oxygen content (in the final solution)
- instability of the collected sample with time
- sensitivity to light
- sensitivity of the collection efficiency to exact operating conditions

In addition to the techniques discussed above, several other techniques have been mentioned briefly in the literature but have not gained a significant following. For example, Kovatsis (1976) describes the application of "indirect atomic absorption spectroscopy to measure H_2S in the environment." Hegyessy employed a AgS ion selective electrode. Tanaka (1978) collected ambient H_2S in 0.1 M NaOH and measured the collected sulfide by monitoring the fluorescence of fluorescein mercuric acetate. The useful range is 0.1 - 4.0 ppbv in air. These methods have been designed primarily to monitor low ambient levels of H_2S, and their application to retort gas has no obvious advantages. Especially considering the availability of instrumental methods, their further development for retort gases does not appear advisable.

4.1.2 Automated Methods

For the purposes of this discussion H_2S monitors can be divided into three main groups:

(1) Instruments which detect H_2S directly (e.g. polarographic cells and non-dispersive infrared analyzers).

(2) Techniques which are inherently sensitive to total S content but which are made selective to H_2S through selective, in-line, sorbent filters (e.g. flame photometric instruments).

(3) Instruments which measure several species simultaneously (gas chromatography, dispersive infrared spectroscopy, and microwave spectroscopy).

In this section I will discuss the first two types of instruments, and reserve discussions of multispecies techniques for sections 4.4 and 4.5. I also discuss here those instruments which measure total S, since H_2S normally is the major S gas. In addition, total S analyzers can in theory be adapted to measure H_2S by using in-line sorbents to remove other S species.

Table 4.4 lists some of the commercially available H_2S instruments. This list is not meant to be complete, but rather to illustrate the major types of instruments available. Table 4.4 was compiled from responses to letters sent to instrument manufacturers soliciting information on their products' abilities to monitor H_2S in stationary sources.

TABLE 4.4. COMMERCIAL INSTRUMENTS FOR MEASURING H_2S AND RELATED SPECIES

Manufacturer/Model	Range	Principle	Comments
Sierra Labs	0-50 ppm	Solid slate sensor	For industrial hygiene
AID, Inc.	> 30 ppb	GC/FPD	Also COS, SO_2, mercaptans
CEA Instruments, Inc.	0.003-10 ppm	Automated wet chemical	Modules available for several other gases
Thermal Electron Corp.	0-5000 ppm	Pulsed fluorescence after conversion to SO_2	SO_2 and total S
Interscan Corp.	0.01-100 ppm	Electrochemical cell-polarographic	
Energetic Science	0-250 ppm	Electrochemical cell-polarographic	
Tracor Instruments	—	GC/HECD	
Wilks Scientific Corp.	—	Dispersive IR Absorption (filters)	
E.I. DuPont	0-2% for H_2S 0-1% for SO_2	Non-dispersive UV Absorption	
Bendix	0-1 ppm	FPD	Measures SO_2, H_2S, or total with appropriate filters
Bendix		NDIR	
Meloy	0.005-10.0 ppm	FPD	Selectivity gained through chemical filters

FPD : flame photometric detector
NDIR: non-dispersive infrared absorption
GC : gas chromatography
HECD: hall electrolytic detector

Of the instrumental monitors shown in Table 4.4, only the polarographic (voltammetric) analyzers are designed to respond to H_2S only. These systems are similar in concept to the classical polarograph except that solid electrodes are used in place of the dropping mercury electrodes. (To distinguish them from classical polarography, such instruments are often referred to as "voltammetric" instruments.) In this instrument the gas diffuses through a selective membrane into a cell where it is oxidized at a polarized electrode. The electrical current is proportional to the rate of diffusion of H_2S to the electrode, and gas concentration is therefore proportional to current. Specificity is attained through selective scrubbing of the incoming gas, by selective diffusion into the membrane, and by setting the polarizing voltage low enough to avoid oxidizing concomitant gases.

Advantages of polarographic systems include simplicity and ease of operation. In some cases the same instrument can be used for more than one gas by simply changing the electochemical sensing cell. Most systems are inexpensive compared to other monitoring systems and are often small enough for portable use. No reagents are required, although the sensing cell must be replaced occasionally.

Disadvantages of the polarographic analyzers include the gradual deterioration of the sensing cell and the associated requirement for frequent calibration. Materials which condense onto or clog the membrane accelerate cell deterioration, may cause erratic results, and require more frequent cell replacement. Cell life under ambient conditions may be up to two years, although longevity upon exposure to retort gases has not been reported.

Of course, the polarographic cell will also respond to any other gas which is oxidized as easily as H_2S and which can diffuse into the cell. While commercially available instruments have been designed to reject interfering gases in ambient air, their rejection of the potential interferences found in retort gas is yet to be established.

For polarographic analyzers the gas typically must be conditioned to 100°F or less and 60 - 70% RH. This is somewhat of a disadvantage for retort gas, which would typically require cooling and drying.

The dynamic range of the commercially available polarographic analyzers are usually more suited for monitoring ambient air or for industrial hygiene applications. This fact probably reflects market demands rather than a technical limitation of the polarographic system, and potential users are encouraged to contact the manufacturer for instruments designed for the higher dynamic range associated with retort gas. Present users are employing dynamic dilution of the retort gas in order to achieve sufficiently low H_2S concentrations.

In addition to the polarographic systems, the automated wet chemical systems also are designed to respond directly to H_2S. (See Table 4.4.) Advantages and disadvantages of these systems include all those associated with the manual colorimetric methods (see above) with few exceptions. In comparison to the manual colorimetric methods, a continuous measurement is possible and labor costs are lower. Nevertheless, automated colorimetric methods are reported to require extensive maintenance compared to other instrumental methods and still demand a continuous supply of reagents.

Although not shown in Table 4.4, argentometric coulometric titration systems for H_2S are commercially available for laboratory use. These presumably could be adapted to field use. Advantages would include long term stability of calibration and low maintenance requirements. Disadvantages include the need to periodically change the scrubbing solution and the requirement of removing other S compounds upstream from the detector. Interferences may be generated by other species which react with Ag^+ ion or can be readily oxidized.

Two instruments in Table 4.4 operate by converting H_2S to SO_2 and then monitoring SO_2, either by pulsed fluorescence or UV absorption.

Specificity for the various sulfur forms can supposedly be gained by the proper selection of chemical filters and converters. For example, the pulsed fluorescent instrument (Thermo Electron Corp.) operates with an in-line chemical sorbent to remove SO_2 followed by a catalytic bed operated at 300 °C to convert H_2S to SO_2. This instrument should therefore be capable of three determinations:

(1) H_2S, as discussed above

(2) SO_2, by shunting both the chemical filter and converter

(3) total S, by completely oxidizing the sample stream

Advantages of this approach include the absence of reagent requirements and--at least with ambient air and thoroughly-burned stack gas--relative freedom from interferences in the measurement of SO_2. It must be emphasized that this technique has not been tested for retort gases, and is yet to be confirmed for this application. Possible problems include spectral interferences or quenching due to organic compounds, or altered behavior of the selective catalytic oxidizer or chemical filters upon exposure to retort gas.

The flame photometric detector (FPD) instruments in Table 4.4 (Meloy, Bendix) respond to the total S content of the sample and gain specificity through the use of in-line sorbents. In theory they should provide a method for measuring total S, H_2S and SO_2 through the judicious selection of chemical filters. A particular advantage of the FPD is that reagents are not required except for compressed gases. (See Lucero et al. [1977] for a review of the mechanical, electrical, and pneumatic design principles of the FPD.)

One shortcoming of the FPD instruments is their low dynamic range (1-1000 ppb) which is better suited to ambient concentrations. Above this range, instrument response becomes non-linear and levels off with increasing S levels. Thus, extensive sample dilution is often required for FPD monitors, a distinct disadvantage for practical reasons, not the least of which is supplying sufficient clean dilution gas.

The response of the FPD is also affected by gases other than S compounds. While not normally problems with ambient air, CO_2 and H_2 in retort gas present potential problems. Reproducible response of the FPD to S compounds requires a constant flow rate of H_2 (manufacturer's data). Since H_2 is a major component of retort gas, what effect do variations in its concentration have on FPD response? Von Lehmden (1978) reported the up to 40% suppression of the FPD response when CO_2 was present at a thousand fold excess. The effect of CO_2 in retort gas, which may reach levels over 20% V/V, is yet to be established.

Quenching of S emissions by hydrocarbons, another major component of retort gas, has also been reported (Thompson, undated). While this potential problem has not yet been investigated for retort gas, Tracor (1978) reports the suppression of the FPD sulfur response in natural gas. Varian Associates claims to have minimized this problem by using two flames in series, the first to combust the sample and the second as a normal FPD (Thompson, undated). Yet it should be emphasized that most hydrocarbon quenching problems arise during the attempt to determine trace levels of S in a hydrocarbon matrix, and that retort gases often contain S gases as major components. In addition, potential users should note that FPD's have been reported with rejection ratios as high as 10,000 for hydrocarbons (Natusch and Thorpe, 1973).

Because the luminescence in the FPD is due to the species S_2, theoretically the photomultiplier current should vary as the square of the S concentration, (S). In fact, the response, R, varies as

$$R = a+b(S)^n \tag{4.1}$$

most accurate work thus requires knowledge of the chemical forms of S which are present in the gas as well as the availability of standards with similar molecular forms.

Since the theoretical value of n in equation 4.1 is 2.0, some FPD's come equipped with a "linearizer" which electronically completes the exponentiation. As pointed out by Burnett et al. (1977), the use of linearizers can lead to errors up to 400% for common S gases since n is not necessarily 2.0. These problems were reported for a single-flame FPD, and may be less severe for dual flame models.

In summary, the FPD as a instrument for measuring total S or H_2S appears to present several difficulties. On the other hand, when used as a gas chromatographic detector most of these problems are alleviated. This use of the FPD is discussed in Section 4.4.

4.1.3 Applications

Owens and McDonald (1979) employed the EPA Method 11 for measuring H_2S during the in situ sideburn at site 12 at Rock Springs. They recommended adding an empty impinger after the H_2O_2 impinger in order to prevent carryover, since they claimed that "prior experience had shown that even minute amounts of this screening solution could drastically affect the outcome of this test."

Prien et al. (1977) analyzed retort gas from the Paraho retort during both direct and indirect operation. Samples were drawn through two impingers containing alkaline solutions of $CdCl_2$ at 0°C. A third impinger was left empty to condense excess water, and a fourth impinger contained silica gel. In most cases the analytical error in measuring the collected sulfide was much less than the total H_2S concentration. No gross malfunction of the method, such as the formation of unexplained deposits or the collection of oily or tarry layers, was reported.

One of the best confirmations of a test method under field conditions is the achievement of mass closure after all streams are analyzed. Such a confirmation was obtained when Goodfellow and Atwood (1974) analyzed H_2S in the product gases from a Fisher assay using gas chromatography. By also analyzing the oil, spent shale, and product oil for total sulfur they were able to achieve 95% closure for S. Since the gas included 20% of the total sulfur, major analytical errors would likely have produced poorer closure. The Fischer assay closely simulates the TOSCO II retorting process, so that these results suggest the efficacy of the GC method for TOSCO II product gas.

Fruchter et al. (1979) measured SO_2 and H_2S at the Paraho direct mode retort using the Interscan polarographic (voltammetric) H_2S monitor. With this instrument the polarizing voltage was changed to distinguish between H_2S and SO_2. However, because the sensor when operated in the H_2S mode responds almost as well to mercaptans, the results for H_2S included mercaptans. Other interferences listed by the manufacturer include H_2 and unsaturated hydrocarbons, although it is unlikely that H_2 is present in sufficient amounts in retort gas to interfere with this technique. The manufacturer claims that unsaturated hydrocarbons can be removed by special sorbents.

Fruchter et al. (1979) also employed a Del-Mar continuous colorimeter to monitor H_2S from the same source. On subsequent days the Interscan instrument and the Del-Mar instrument reported 2800 and 2400 ppm H_2S. respectively. Although no samples were analyzed in parallel, these results are encouraging since plant operation was supposedly uniform throughout.

In either case, no unusual operating problems were reported. However, the retort gases did require dilution in order to be within the dynamic range of either instrument. In addition, it was not clear whether any cooling or drying was required upstream from the analyzers. These investigators also measured S in the raw and spent shale, product oil, and wastewater, and were able to obtain 93.5% closure. Since 12.7% of the S was partitioned into the gas phase and 80% into the spent shale, closure was limited by the accuracy of the S measurement in the latter two materials. In summary, while the results of Fruchter's measurements at the Paraho retort are encouraging, they are far from conclusive regarding the viability of these two instruments for measuring H_2S.

McDonald (1980), at the Laramie Energy Technology Center (LETC), has been using a suite of instruments to monitor H_2S, SO_2 and total S in product gas from their 150 ton simulated in situ retort. SO_2 is monitored with a Meloy model SA 160-2 and a Dupont model 411. The Meloy instrument is based on a flame photometric detector and achieves specificity through the use of selective sorbents to remove interfering gases such as H_2S. The Dupont instrument is based on non-dispersive UV absorption. H_2S is monitored by a Energetics series 7000 Ecolyzer, which is based on a polarographic (voltammetric) cell. Total S is monitored by a Meloy model SA 202-2, which is also based on a flame photometric detector. Sample pretreatment for all analyzers includes gas cooling and drying.

The principal operational difficulty reported by McDonald is that excessive dilution of the gas is required to maintain concentrations within the dynamic range of the instruments. (With the exception of the Dupont instrument, the remaining analyzers are mainly for ambient applications.) Stability of the flame in the Meloy instrument is occasionally disrupted by the changing composition of the retort gas. In addition, negative concentrations of H_2S have been observed, a result not yet been explained.

4.2 Sulfur Dioxide

Although SO_2 is apparently not a major form of S in retort gas, its measurement may nevertheless be important for two reasons: First, total S or H_2S can be oxidized and detected as SO_2. This interpretation is attractive because of the abundance of commercially available SO_2 monitors which can serve as the basis for instruments designed more specifically for retort gas. Second, as a gas which is not removed effectively by H_2S control equipment, SO_2 measurements may be important as a diagnostic tool.

4.2.1 Methods

The measurement of SO_2 in ambient air and in thoroughly combusted gases has been reviewed extensively and need not be repeated here. I refer the reader to Barras (1973) for a review of instrumental stack monitors and to LBL (1976) for a review of commercially available instruments. LBL also reviews the principles of operation of most common instrumental and manual methods for SO_2. APHA (1977) and Leithe (1970) give details of several procedures for SO_2. (See Table 4.5 for additional references on methods for SO_2.)

Table 4.6 summarizes some of the most common methods for SO_2. Because of the extensive reviews which are available, these methods will be discussed only very briefly, and with emphasis on oil shale. The reader should note that these methods have been tested primarily for ambient or stack (combusted) gases, and their extrapolation to retort gases is questionable. The interferences listed in Table 4.6 thus represent potential but unconfirmed problems. For example, although polarographic analyzers respond to any gases which are more easily oxidized than SO_2, it is not clear whether such gases are a problem in retort gas or whether the present instrument design successfully counteracts such potential interferences. On the other hand, there are likely interferences in retort gases which have not yet been discovered, simply for lack of complete testing.

TABLE 4.5. REFERENCES FOR SULFUR DIOXIDE

Use of tunable diode lasers	Reid et al. (1978)
Absorption in H_2O_2 solution. EPA Method 6	PEDCO (1977)
Commercially available instruments	LBL (1976)
Collection in H_2O_2 and in perborate	AIHA (undated)
Practical field guide	Benchley et al. (1974)
Selection of source monitors	Barras (1973)
Details of standardized methods: colorimetric, titrimetric, conductimetric, amperometric	APHA (1977)
Advanced methods	Stevens & Hoget (1974)
Details of several manual procedures	Leithe (1970)

TABLE 4.6. OPERATING FEATURES OF METHODS FOR MEASURING SULFUR DIOXIDE

Method	Comments
(1) EPA Method 6 $SO_2(g)+H_2O_2(\ell)\rightarrow H_2O + SO_4^=$ $SO_4^=$ by Thorin titration (Other methods for $SO_4^=$ can be used.)	Range : 3- 90,000 mg/m^3 Interferences: NH_3, sulfides, soluble sulfates, Wackenroder's reactions. Application: stack monitoring
(2) West-Gaeke Method	EPA reference method for ambient air.
$SO_2 + K_2HgCl_4\rightarrow Hg(SO_2)Cl_2 + 2KCl$	Low bias in results
pararosaniline + $CH_2O + SO_2\rightarrow$dye	Range: 0.01-~3 ppm Optimized for ambient air Requires skilled operator Tempermental Interferences: NO_x Time consuming
(3) Iodometric Method	
$2H_2O+SO_2 + I_3^-\rightarrow 3I^- + H_2SO_4 + 2H^+$ Measure change in I_3 (starch) absorbance	Interferences: oxidants and reductants
(4) Fluorescence of SO_2-dye complex	Highly sensitive For ambient or pristine atmospheres
(5) Conductimetric analyzers with selective, in-line, chemical filters	Range: 0.01-8,000 ppm Interferences: any species forming or removing ions (e.g. NH_3, H_2S, organic acids)
(6) Coulometric (Amperometric) Analyzers of various design e.g. $2Br \rightarrow Br_2 + 2e$ $2H_2O + Br_2 + SO_2\rightarrow H_2SO_4 + 2HBr$	Stable calibration Minimal maintenance Interference: oxidizing and reducing agents
(7) Polarographic (voltammetric) analyzers chemical oxidation at a "polarized" electrode	See Section 4.1.2 Simple operation No reagent requirements Selectivity depends on Chemical filters, membrane selectivity, and selection of the polarizing voltage

TABLE 4.6 (continued)

Method	Comments
	Interferences: compounds more easily oxidized than SO_2 Most are designed for ambient air
(8) Flame Photometry emission of the S_2 species at 394 nm	See Section 4.1.2 Sensitive Responds to all S compounds Interferences: H_2, CO_2, hydrocarbons, other S-containing compounds
(9) Non-dispersive infrared spectrometers	No reagents Interferences: other IR absorbing species Range: > 10 ppm Restricted mainly to stack monitoring
(10) Non-dispersive ultraviolet spectrometry	For stack monitoring Interferences: Species absorbing near 280 nm
(11) Dispersive infrared spectrometers	Range: 0.1-3000 ppm Capable of multi-species monitoring Interferences: other IR absorbing species High calibration drift
(12) Second derivative UV spectrometers	Multispecies capability
(13) Ultraviolet fluorescence Fluorescence at 340 or 415 nm	Available as either source or ambient monitors Relatively free of interferences under normal ambient or stack conditions Interferences: compounds fluorescent at 540 or 415 mm fluorescent quenchers such as H_2O

Method (1) in Table 4.6 is widely employed as the compliance method for SO_2 stack emissions. The sampling train called for in this method consists of a probe followed by four bubblers cooled to 0°C. The first bubbler contains 80% isopropanol to remove SO_3, the third and fourth contain 3% H_2O_2 for collecting SO_2, and the fourth bubbler is empty. Although the EPA protocol calls for determining the collected SO_2 (after conversion to $SO_4^{=}$) by the Thorin titration method, any number of other finishes, ranging from acid/base titrations to ion chromatography, are technically feasible.

One component of retort gas which is likely to interfere in this method is NH_3, which can form $(NH_2)_2SO_3$ in the isopropanol bubbler. Other sulfides, such as H_2S, can also be oxidized to sulfate in the H_2O_2 bubbler to give a positive interference. Of course, Wackenroder's reaction (Section 3.1) likewise may remove SO_2 in the isopropanal solution or convert H_2S to sulfur oxides in the H_2O_2 solution.

The second method in Table 4.6 is designed primarily for ambient air, and even under such conditions has a reputation for being highly sensitive to the skill of the operator. Its application to retort gas has no apparent benefit.

The remaining comments in Table 4.6 should be self explanatory. Based on the available data, no single method can be selected as superior or uniquely suited for retort gas, and each method has potential interferences. Obviously, methods which require no reagents and minimum sample pretreatment are preferred. Especially because of the presence of NH_3 in retort gas, exposure to liquid water in the sample train (e.g. in a cooler/dryer) is likely to remove SO_2 as $(NH_3)_2SO_3$. Analyzers which depend on a non-specific response, such as conductimetric analyzers, may work well under ambient or stack conditions, but their applicability to retort gas is doubtful because of the large number of potential interferences not found in other gas streams.

4.2.2 Applications

Prien et al. (1977) used the standard EPA method 6 for determining SO_2 in both direct and indirect process gas at the Paraho retort. They concluded that the analytical errors in measuring the collected SO_2 were minor compared to the concentrations they encountered. Parallel samples were not collected so that no statement can be made regarding the precision of the method. During continuous operation of the plant over a four day period, the measured SO_2 values varied from 14-23 ppmv, which can either be attributed to actual variations in SO_2 or to random errors in the method. Interferences by NH_3 were not addressed.

Fruchter et al. (1979) measured SO_2 using an interscan polarographic H_2S monitor in which they varied the retarding potential in order to distinguish H_2S and SO_2. With and without prior dilution of the sample stream they achieved similar results.

Owen and McDonald (1979) measured the SO_2 in the stack gases produced by the in situ retort at Rock Springs site 12. In order to remove the interference due to NH_3, a bubbler containing 0.1 M HCl was placed upstream from the normal EPA method 6 sampling train. No operational problems, such as the formation of oily layers or dark precipitates, were reported. Because no samples were collected in parallel, no information is available on the precision of this method under field conditions.

The Laramie Energy Technology Center (McDonald, 1979) uses a DuPont model 411 SO_2 analyzer and a Meloy model SA 160-2 to determine SO_2 in retort gases from their simulated in situ retorts. The DuPont analyzer is based on non-dispersive UV absorption and the Meloy uses a flame photometric detector with appropriate chemical filters. The comparability of these two instruments has not yet been reported.

Other developers are currently using gas chromatography with S-selective detectors for measuring SO_2 as well as other S gases. These are discussed in section 4.4.

4.3 Ammonia (and other N-containing gases)

Ammonia is important in retort gas because of its commercial value and its deleterious effect on certain types of S control equipment. In addition, the presence of ammonia and other N compounds in fuel gas increases formation of NO_x upon combustion. Consequently, currently proposed regulations on NO_x emissions take into account the level of N compounds (other than N_2) in the fuel gas.

4.3.1 Methods

Table 4.7 summarizes a number of references which describe methods for measuring gaseous NH_3. (Methods for aqueous NH_3 are discussed in Chapter 3.) Many of the methods described in Table 4.7 are optimized for ambient or near ambient levels of NH_3 with the corresponding emphasis on low detection limits and preservation of sample integrity. However, when the sampling and interference problems associated with retort gas are properly accounted for, it is likely that at least some of these methods can be adapted. Table 4.7 also contains references for other N-containing compounds, although these will not be discussed further here.

The most common manual methods begin by absorbing NH_3 in a dilute acid, typically 0.1 N H_2SO_4, followed by a variety of possible finishes. For example, the NIOSH (1977) calls for the collection of NH_3 in 0.1 N H_2SO_4, followed the potentiometric (i.e. ion selective electrode) detection of the collected NH_3. Assuming a working range of 0.1-1000 mg/ml for the ammonia electrode, a solution volume of 10 ml, a sample flow rate of 100 ml/min, and a sampling time of 100 minutes leads to a working range of 0.1-1000 mg/m^3 in the gas sample, adequate for retort gas, especially since the absorbing solution can be diluted. Major advantages of the ion selective electrode (ISE) are ease of use and relative freedom from interferences. (The major interferences with the ISE are volatile amines, which are insignificant compared to NH_3 in retort gas.) However,

TABLE 4.7. AMMONIA AND OTHER N-CONTAINING GASES

General Methods

Manual, standardized methods for ambient and industrial atmospheres	APHA (1977) Leithe (1977) NIOSH (1977)
Pyridene-pyrazolene colorimetric method. Collection with H_2SO_4-impregnated filters	Okita & Kanamori (1971)
Collection on Ag/Mn impregnated filters	Eguchi & Hirofumi (1977)
Automatic, continuous monitor based on pH electrode and aqueous scrubber	Steczkowski (1979)
Direct UV absorption at 201 nm	Cresser (1977)
Direct UV absorption	Gunther et al. (1956)
UV absorption with a diode laser source	Reid et al. (1978)
Monitoring over long pathlengths by absorption of CO_2 laser radiation	Artemov (1977)
Microwave absorption	Hrubresh (1977)
Potentiometric detector for gases	Nicholas (1973)
Conversion to NO with chemiluminescence finish	Aneja et al. (1978)
Conversion of NH_3 to NO on Pt catalyst; IR or chemiluminescence finish	Herose et al. (1979)
NH emissions from a N_2/Ar flame	Butcher & Kirhfught (1978)
Gas chromatography with a Hg-sensitized luminescence detector	Harker (1975)
Gas chromatography of furnace gases	Derge (1965)
Gas chromatography with a thermal conductivity detector	Sims (1974)

TABLE 4.7 (continued)

GC detector for NH_3	Poppet et al. (1978)
NH_3 at the Paraho Retort	Cotter et al. (1978)
The effect of retorting conditions on ammonia formation	Maier et al. (1924)
Ammonia in a true in situ retort	Owen & McDonald (1979)
N-Containing Gases	
NO_x in combustion streams by collection in H_2O_2/H_2SO_4	PEDCO (1977)
NO_2, NO, HCN in the atmosphere: a review of methods	Leithe (1970)
NO_x in combustion streams: practical suggestions	Benchley (1974)
HCN by collection in NaOH solution	AIHA (undated)
NO_2 and NO: review of commercial instruments	LBL (1977)
HCN, CS_2 in the workplace	NIOSH (1979)

the membrane in the ammonia is easily fouled by oils and tars, and this feature remains a potential problem.

Other common methods for measuring NH_3 in the absorbing solution include the nitrite method, the indophenol method, and Nessler's method (APHA, 1977; Leithe, 1971: Okita and Kanamori, 1971). In the nitrite method, NH_3 is oxidized to NO_2^- with HOCl, and the nitrite is then converted to an azo dye and measured colorimetrically. Known interferences include CHO, NO_2, hydrolyzable amino compounds and alkali earth salts. The range of this method is approximately 14-220 ng/m^3; higher values should be accessible by diluting the sample collection solution.

In the indophenol method NH_3 is converted to a indophenol dye, which is then measured by spectrophotometry. Interferences include NO_2, SO_2, CHO, Fe, Ci, Mn, and Cu, although several of these can be masked by the addition of EDTA. A typical range for this method (with no dilution of the absorbing solution) is 20-700 ng/m^3.

Nessler's reagent has been widely used in the past for the determination of collected NH_3 but has now been largely replaced. (APHA, 1977; Leithe, 1971). Interferences include H_2S, and CHO. The working range has been reported as 0.02 to 80 mg/m^3.

In place of aqueous solutions and impingers, solid sorbents are occasionally used for sample collection. For example, Okita and Kanamori (1971) selected H_2SO_2 impregnated filters for the collection of NH_3 in the urban atmosphere, a preference based on their observation that the collection efficiency of H_2SO_4 bubblers gradually decreased during the course of sample collection. Eguchi (1977) also describes a passive sampling device consisting of a filter medium which had been loaded with Ag and Mn salts as well as glycerin. The effectiveness of the latter combination is somewhat doubtful considering the high levels of H_2S in retort gas. Advantages ascribed to solid samples are ease of use and higher sample collection rate.

Steczhowski et al. (1975) automated a wet chemical technique to provide continuous process control. Their device consisted simply of an aqueous scrubber and pH meter. Adaptation of this technique to retort gas would presumably require consideration of other water soluble gases such as CO_2, SO_2, H_2S, and organic acids.

UV absorption appears an attractive--and as yet untested--alternative for measuring NH_3 in retort gas since sample drying or cooling could presumably be avoided and the absorption spectrum could be recorded directly. NH_3 absorbs strongly in a series of sharp bands between 188 and 224 nm (ε= 10-4000 l mole^{-1} cm^{-1}), which should be ideal for measuring NH_3 in the concentration range 10 ppmv to 1% (Gunther et al., 1956). Of course, many other compounds also absorb in this region, and the applicability of this technique for retort gas must yet be established. The sharp absorption spectrum in NH_3 ranges is especially valuable, since this aids in the rejection of broadband background absorption by such techniques as second derivative spectroscopy.

Table 4.7 lists four studies of the measurement of NH_3 by direct UV absorption. Gunther et al., (1956) used a simple Beckman DU spectrophotometer tuned to 204.3 nm to measure NH_3 in the gas phase in the range 7-1000 ppmv. Cresser (1977) similarly was able to quantitate NH_3 evolved from soil samples in the range 0-500 ng. Reid et al. (1978) and Artemov et al. (1977) both used laser sources for detecting NH_3 in ambient air by UV absorption.

Microwave spectroscopy has been proposed as a method for NH_3 because of the easily resolved series of lines centered at 23 GHz, which are due to an inversion oscillation. Using the absorption line at 23.870 GHz Hrubresh (1977) designed a field model suitable for monitoring NH_3 in the industrial workplace (range = 0.1-100 ppm). This instrument required a semi-permeable membrane to preferentially enrich NH_3 over the other components in ambient air. (Microwave spectroscopy is discussed more fully in Section 4.5.2.)

NH_3 can also be determined by chemiluminescence after catalytic conversion to NO (Aneja et al., 1978). The commercial availability of such instruments, which can then also measure NO and NO_2, has increased the popularity of this approach, at least for combusted stack gases.

Commercially available instruments currently cover the range 0.1 ppb to 1%, more than adequate for monitoring retort gas. Water vapor and CO_2, have been reported as interferences, although this has not been consistently observed (LBL, 1976). As with other methods which have been optimized for criteria pollutants in ambient air, little data is available establishing the validity of this method for retort gas.

In a N_2/H_2 diffusion flame the introduction of NH_3 generates a broadband emission at 336.0 nm, presumably due to chemiluminescent emissions from the species NH. Bulcher and Kirkbright used this phenomenon to measure NH_3 solution at levels down to 0.2 ng/ml, but the suitability of the technique is clearly not established for complex samples such as retort gas.

NH_3 in an inert carrier gas has also been determined by Hg enhanced luminescence (Harker, 1975), based on the broadband emission centered at 345 nm which occurs when a mixture of Hg vapor and NH_3 are irradiated in the UV region. A similar phenomenon occurs with Cd vapor. This approach is highly subject to interferences due to hydrocarbons, amines, aldehydes, and water, and would therefore require a clean chromatographic separation prior to detection.

The gas chromatographic separation of NH_3 has been difficult because of the tendency of this substance to disappear onto column walls, packings, and tubing. Nevertheless, several workers have reported successes on various substrates. For example, Sims (1974) separated NH_3 in water samples on a specially treated column of Carbowax 20M on Teflon, and was able to quantitate NH_3 in the range 0.1-6% v/v. For NH_3 in a mixture of ethylene and N_2, he used phasepack Q packing heated with 8% w/w KOH and

10% w/w Versamide 900. Using a thermo-conductivity detector he was able to operate in the range 2-10% v/v NH_3, although better detectability should be feasible using modern thermo-conductivity detectors.

For ambient air levels of NH_3, Harker (1975) recommends a Teflon column packed with chromosorb 104 treated with THEED (optional). Derge (1965) also discusses the application of gas chromatography to the analyses of furnace atmosphere.

While the thermo-conductivity detector may be somewhat insensitive as a detector for NH_3 at the levels expected in retort gas (detection limit $\cong$ 0.1% v/v), newer N-selective detectors should provide more than adequate detectability. For example, electrolytic conductivity cells can detect less than a nanogram of N and therefore should be adequate to detect NH_3 in the ppm range.

4.3.2 Applications

NH_3 is a major component of retort gas and in some processes may be a commercially valuable by-product. For this reason its production as a function of retorting conditions has been widely studied (Maier, et al. 1924; Jones, 1976; Owen and McDonald, 1979). While the methods of analysis are not normally described in detail, it is usually safe to assume that the manual, wet chemical methods have been applied, especially in the older studies.

Cotter et al. (1978), however, did describe in somewhat more detail the sampling and analysis procedures which they used at the Paraho retort. They employed four impingers in series cooled in an ice bath. The first typically contained d.i. H_2O, the second 5% HCl, the third was empty to catch any spill-over, and the last impinger contained silica gel to dry the gas stream. Sampling rate was 200 ml/min. They reported that the analytical error in measuring the captured NH_3 was much less than the total ammonia concentration. No data was available on the precision of the total sampling and analysis scheme.

4.4 Gas Chromatography

Gas chromatography has been used perhaps more extensively than any other technique for analysis of the various S-gases in the atmosphere. This situation arises because of the availability of highly selective and sensitive S detectors which distinguish S and non-S containing gases. The advent of highly inert materials, such as Teflon, also permits the handling of gases such as H_2S, which otherwise would react irreversibly with columns and sample lines. The general simplicity of gas chromatographs as well as widespread familiarity with this technology also encourages such application.

Table 4.8 lists references describing the gas chromatographic determination of S gases in various environmental samples. As can be seen, most references treat the determination of very low levels of S gases, such as those occurring in the stratosphere or in ambient air. These investigators thus emphasize preconcentrating the sample, improving detectability, and avoiding loss of the minute mass of collected material.

4.4.1 Sampling

Adapting such methods to retort gas presents quite the opposite problem. The high levels of S compounds can easily exceed the dynamic range of the detector, and methods of injecting sufficiently small samples must be considered. Because gases such as SO_2 can easily dissolve in the basic condensate produced by cooling the gas, retort gas should be injected directly into the GC with no pretreatment. As discussed below, a heated sample line and a sample loop should be sufficient for most retort gases.

When retort gas cannot be injected into the GC, it may be necessary to use a sample container for transfer and temporary storage. Such gas sampling techniques described in the literature include:

- cryogenic traps
- rigid glass or steel containers
- inflatable plastic bags
- sorbent cartridges

Cryogenic trapping has been widely used for sampling pristine air, such as is found in the stratosphere. For example, Bramman et al. (1978) collected H_2S and other S compounds in air cryogenically with gold-coated glass beads. Using similar cryogenic techniques, Inn (1979) collected COS and CS_2 in ambient air. Inn reported that COS was stable for several days when kept in the cryostat.

Farwell (1979) used a cryogenic U-tube filled with polysiloxane-coated glass beads at liquid O_2 temperature. He also reported that the anti-seizing compounds found on fittings are a strong sorbent for S compounds and must be removed. FEP Teflon loops and column packing beads were also evaluated as trap materials, but exhibited unsatisfactory memory effects. Each of these sampling techniques was designed to be compatible with a GC injection system for final analysis.

In western oil shale areas the levels of S compounds in ambient air are typically below the detection limits of most commercially available instruments. Cryogenic enrichment may therefore be appropriate for monitoring ambient air in these locations. However, this approach seems particularly inappropriate for retort gases because of the large volume of water vapor contained in retort gas and because of the need to avoid exposing the gas to liquid water.

Gangwal et al. (1979) report on the use of glass containers to collect samples from stacks and process lines, and include descriptions of valves, connectors, and tubing. Special features of their system include the ability to sample stacks at either sub- or super-ambient pressures and the capacity to store samples at 50°C until analysis. By means of a special sample transfer system, samples were injected directly from the glass buret into a GC without dilutions with air.

TABLE 4.8. GAS CHROMATOGRAPHIC TECHNIQUES FOR S-CONTAINING GASES

Gas Chromatographic Techniques	
S gases in the atmosphere with FPD detector	APHA (1977)
Description of the FPD detector	Lucero and Paljug (1974)
Commercially available instruments	LBL (1976)
Element selective detectors	Natusch & Thorpe (1973)
Reduced sulfur compounds in air; Cryogenic trapping and capillary columns	Farrell et al. (1979)
Gaseous sulfur compounds from fossil fuel conversion	Gangwal et al. (1979)
General discussion: instrument requirements	Thompson (undated)
CS_2 in air	Godin (1979)
COS in the stratosphere; collection & analysis	Inn (1979)
Various S gases in the atmosphere	de Souza & Bhatia (1976)
H_2S, COS, CS_2 & SO_2 in hydrocarbon streams	Pearson & Hines (1977)
COS and CS_2 in the atmosphere	Sandalls & Penkett (1977)
H_2S in air; preconcentration during sampling	Braman et al. (1978)
H_2S, COS, SO_2, CH_3SCH_3 in air	Walker (1978)
Electrochemical detector for SO_2, SO_3, H_2S, CH_3SH, and COS	Chamberland & Gauther (1977)
Electrochemical detector sensor for SO_2, NO, CO, and NO_2	Blurton & Stetter (1978)
Column and FPD improvements	Bruner et al. (1976)
Comparison of GC and classical methods	Fradkin & Petrov (1978)
CS_2 with an EC detector	Pinigina (1977)

TABLE 4.8 (continued)

Sulfur compounds and CO_2 in hydrocarbon streams with an electrolytic conductivity detector	Schiller & Bronsky (1977)
Effect of S compound type on FPD sensitivity	Doehler et al. (1977)
Errors in using the FPD	Burnett et al. (1977)
H_2S at trace levels	Steller et al. (1977)
Trace sulfur compounds by standard additions	Marcelin (1977)
Interferences in the coulometric S detector	Cedergren & Suden (1977)
Sulfur compounds with a coulometric detector	Martin & Grant (1965)
S gases in the air by GC/FPD	Stevens & O'Keefe (1970)
CS_2 using a PID	Smith & Krause (1978)

FPD = flame photometric detector

EC = electron capture detector

PID = photoionization detector

Gangwal et al. tested the stability of COS, CH_3SH, CS_2, C_2H_6S, and thiophene in coal gas using this system. Over a 100 hour period, changes were less than 5%. Similar data for H_2S, SO_2, COS, and CH_3SH are reported for ambient air samples, although H_2S did decay significantly after 100 hours.

Plastic bags, typically constructed of laminated materials such as Teflon, aluminum, and Mylar are recommended because of convenience and ease of handling. However, several problems remain, including the condensation of water vapor and concomitant dissolved species, diffusion of sample through the walls, and reactions with the walls (Krun et al., 1979). In my opinion, polymeric bags should be considered unproven for sampling reactive or trace components of retort gas.

Porous polymers such as XAD-2 and TENAX-GC have been widely used as sorbent traps, especially for organic compounds. The principal advantage to this system is ease of sample collection and shipment. A number of investigators have examined the retention of individual organic compounds by porous polymers; however, the behavior of such polymers when exposed to a gas mixture is less clear (Pellizari et al., 1975; Russell, 1975; Russell et al, 1977).

For example, Stephen and Smith (1977) have shown that porous polymer resin can retain non-polar compounds preferentially while allowing polar compounds to escape. Although porous polymers may be adequate for non-reactive organic materials, they would not be recommended for reactive gases such as H_2S, SO_2, and mercaptans. Indeed, a major problem in the gas chromatographic analysis of such compounds is their reactivity with support and column materials, and similar reactions with sorbent materials are likely (Stevens and O'Keefe, 1970). Thus, sorbent resins may be convenient for some classes of compounds but do not necessarily represent a universal, non-selective collection media.

On the other hand, the use of sorbent tubes for the collection of specific compounds in industrial atmospheres is common. Thus, Smith and Krause (1978) discuss the use of charcoal tubes for the collection and analysis of CS_2 in the industrial atmosphere, and Godin (1979) discusses the use of hexamethylphosphorotriamide and sodium azide on chromosorb W for the same purpose. However, in such cases the sorbent material is tested for a specific compound and is not necessarily applicable to others.

4.4.2 Column Materials and Conditions

Gas chromatographic separations of the major inert gases such as N_2, CO, CO_2 are well established and need not be discussed here. Similarly, molecular weight profiling of light hydrocarbons is one of the first applications of GC, and is a technique which should work readily for retort gases as well.

Of special interest in this section will be separations of S gases, principally for detection by a flame photometric detector (FPD) or in some by other S selective detectors. In reviewing the case studies described below, the following guidelines which columns must meet should be considered:

(1) S species must be separated from each other; H_2S and COS (bp = -61.8 and 48°C) tend to co-elute and therefore present a special problem.

(2) S species must be separated from major peaks of CO_2, CO, or hydrocarbons to avoid interferences in the FPD.

(3) Special valves, tubing, sample lines, and column materials must be selected to avoid sample losses.

(4) Sudden bursts of H_2 or hydrocarbons can extinguish the FPD--thereby requiring recalibration--and should therefore be avoided.

Besides the S gases, reactive N gases such as NO and NH_3 have also been separated by gas chromatography. However, this is a rather minor application and will not be discussed extensively here.

In one of the earlier descriptions of the gas chromatographic determinations of S compounds with specific element detectors, Martin and Grant (1965) used a silicon rubber column for measuring S in petroleum products. Although a S profile was obtained up to C_{20}, only the lightest compounds could be resolved.

In 1970 Stevens and O'Keefe discussed the difficulties in developing sufficiently inert columns, valving, and a sampling system for measuring low ppb levels of SO_2, H_2, CH_3SH, and CH_3CH_2SH in ambient air. They selected a 34' x 0.085 id FEP Teflon column packed with polyphenyl ether and phosphoric acid on 40/60 M Teflon. Temperature programming was apparently unnecessary.

De Souza and Bhatia (1976) describe a GC system for separating H_2S, COS, SO_2, CH_3SH, and $(CH_3)_2S_2$ at ambient levels. Their column of choice was 3 m x 3.2 mm Teflon packed with pre-treated Porapak QS. Sampling valves were of carpenter 20 stainless steel. For the separation of H_2S and COS the column was kept at 140°C, and then programmed at 40°C/min to 230°C for heavier compounds. SO_2 was not successfully determined because of irreversible losses.

Sandalls and Penkett (1977) measured CS_2 and COS in atmospheric samples using three separate columns. COS was separated using a 50 cm x 4 mm id glass column of 80/100 M Porapak QS at 50°C. CS_2 was determined on two separate columns: a 2 m x 4 mm id glass column containing 10% Triton X 305 + 0.57 H_3Po_4 on 70/80 M acid washed diatomite M at 35°C and

(2) a 1 m x 4 mm id glass column with 25% 1,2,3-Tris (2 cyanoethoxy) propane on 60/80 M acid-washed diatomite C at 40°C. Also, in 1977 Sheller and Brovsky described the use of two columns for separating H_2S through butyl mercaptans in petroleum products. The first column was 3' x 1/4" od stainless steel with acetone washed Porapak QS 80/100 M, which was temperature programmed from 60°C to 160°C. The second column was 36' x 1/8" Teflon containing polyphenyl ether and H_3PO_4 on 40/60 M Teflon powder operated isothermally at 80°C.

Pearson and Hines (1977) developed a master scheme for measuring H_2S, COS, CS_2, and SO_2 in a variety a samples including specifically inert gases and water vapor, methane-ethylene mixtures, and propane-butadiene mixtures. Quantitative analyses required the separation of the S compounds from the hydrocarbon materials in order to avoid interference in the flame photometric detector (FPD). In addition, the hydrocarbons would often extinguish the flame in the FPD which would then require recalibration.

For this range of samples Pearson and Hines required four separate columms, each made of 3 mm od stainless steel which had been deactivated with Siliclad 3%:

- 3 m, with 5% polyphenyl ether + 0.4% H_3PO_4 on chromosorb G, 80/100 M
- 1.8 m with treated silica gel
- 1.8 m with 5% silicone QFI-6500 on Porapak QS
- 7.3 m with 10% polyphenyl ether + 0.4% H_3PO_4 on chromosorb G

The first column is programmed from 70-200°C and serves to qualitatively screen the sample for compounds up to diamyl disulfide. The second column is most widely used and can separate H_2S, COS, CS_2, and SO_2 from each other but not necessarily from hydrocarbons $\geqq C_3$. A combination of columns is required to quantitate all four species in the three matrices studied. This paper amply illustrates the difficulties in adequately separating hydrocarbons from the S compounds in hydrocarbon matrices. Of particular value was a dual FID/FPD detector which permitted the detection of hydrocarbons as well as S-compounds. With artificial gas mixtures Pearson and Hines claimed a precision of 3.3% for H_2S and 1.67% for COS.

This system was primarily designed for S gases in the range 1-50 ppm. Above this range the FPD responded poorly, while below this range stainless steel columns are not normally used. Since the S hydrocarbon ratio in retort gas is much higher than the ratios investigated by Pearson and Hines, hydrocarbon interferences should be less severe.

Walker (1978) used a 1 m x 1/4" od FEP Teflon column packed with Tenax GC to separate H_2S, COS, SO_2, CH_3 SH, and $(CH_3)_2S_2$ at levels of 1-100 ppm in air. He claimed that this column was particularly easy to pack and required no pretreatment. Nevertheless, several injections were required before a reproducible response was achieved.

In 1977 Stetter used a 6' x 1/8" od FEP Teflon column packed with chromosil 310 for the measurement of H_2S in air. In addition, he recommended the use of all Teflon gas sampling valves and associated parts. Inn et al. (1979) also used a chromosil 310 column to separate COS in stratospheric samples, as well as a Porapak QS in a 1/8" stainless steel column and a Porapak QS with H_3Po_4 in a Teflon column for the same purpose.

Farwell et al. (1979) attacked the problem of hydrocarbon interferences in the FPD by using a higher resolution, wall coated open tubular column (WCOT) in place of the packed columns which have been described above. They first evaluated a 30 m x 0.25 mm WCOT columns with SD-30, carbowax 20M and OV-17, but each exhibited excessive tailing. WCOT glass columns of 30-38 m length were finally selected. All glass parts and columns required deactivation in order to avoid sorptive losses. This column separated H_2S, COS, CH_3SH, CH_3SCH_3, CS_2, $(CH_3)_2S_2$ and other compounds from each other as well as from hydrocarbon interferences in ambient air samples. Column temperatures were programmed from -70 to 100°C, and about 15 minutes was required for each chromatogram.

Harwell evaluated this column in comparison to column packings of Triton x-305, Teflon powder with polyphenyl ether and H_3PO_4, deactivated silica gel, graphitized carbon black with H_3PO_4, and acetone treated Porapak QS. Advantages he claimed for the WCOT columns included smaller surface area (hence fewer sorptive losses), better separation from hydrocarbon interferences, lower pressure drops, and the better resolution of H_2S and COS.

In summary, it is not clear that a single column will suffice for separating both the minor and major sulfur species in retort gas as well as the interfering hydrocarbons, carbon monoxide, and carbon dioxide. Nevertheless, the number of columns and the number of successful separations with similar samples is quite encouraging.

4.4.3 Detectors

The flame photometric detector (FPD) is clearly the most common type of S-selective GC detectors. This detector has already been discussed in section 4.1.2 as a total S monitor, and the same comments apply here. By way of review, salient features include:

- low dynamic range (10^{-10} - 10^{-7} g/sec)

- freedom from reagent requirements except for compressed gases

- fast response compared to most other S detectors

- instability of the flame upon exposure to combustible gases such as H_2, CO, and hydrocarbons

- selectivity ratios for S compounds (as compared to hydrocarbons) of up to 10,000

- suppression of the S signal by CO_2 or hydrocarbons

- dependence of S response upon molecular form

The low dynamic range is best suited for ambient levels of S and for retort gas. Care must be taken to achieve sufficiently small samples. The freedom from reagent requirements is especially desirable when operating under field conditions, although compressed H_2 cylinders may be prohibited in some locations. The comparatively fast response permits the use of WCOT or capillary columns whenever they are needed to separate interfering hydrocarbons from the S compounds.

The instability of the flame upon exposure to combustible gases arises from the requirement of operating the FPD with a fuel-rich flame, often verging on extinction. The addition of small amounts of other fuel gases can therefore disrupt the flame equilibrium, thereby changing its sensitivity or even extinguishing the flame altogether, in which case an entire re-calibration may be necessary. Since retort gas typically includes H_2, CO, and hydrocarbons in amounts ranging from 0.1 to 25%, the effects of these major peaks must be considered.

The selectivity of the FPD means that up to 10,000 parts of a hydrocarbon gives the same response as 1 part of S. However, at much lower levels hydrocarbons and CO_2 quench the S signal, implying that hydrocarbon and S peaks must be cleanly separated for quantitative analyses.

The dependence of sensitivity upon molecular form requires that each S compound be calibrated separately for quantitative work. Varian Associates has attempted to minimize this inconvenience by placing two flames in series, the first to combust all S forms to common fragments, and the second to provide the luminescent signal. This arrangement was also designed to minimize flame extinction and hydrocarbon interferences. However, Gangwal et al. (1979) report that even with the Varian dual-flame detector, the FPD remains measurably sensitive to molecular form.

Pearson and Hines approached this same problem by using a FPD in combination with a flame ionization detector (FID). This arrangement clearly indicated the presence of co-eluting hydrocarbons, which could then be removed by column modification. They reported that re-calibration of the FPD was required every four hours for quantitative work. With a one ml sample loop, gases containing over 50 ppm of S gases required dilution in order to remain within the dynamic range of the FPD. They reported a precision of 3.3% RSD for H_2S and 1.6% RSD for COS in synthetic mixtures of light hydrocarbons (C_1 - C_4).

In addition to the FPD, other GC detectors which operate on the principles of polarography (voltammetry), electrolytic conductivity, photo-ionization, and coulometry have been reported. Thus Stetter (1976) and Blurten et al. (1978) used a PTFE diffusion bonded electrode for a polarographic GC detector. The lower detectable limit was 5 ppb (10^{-12} g with a 1 ml sample loop) for H_2S, which is approximately the same as for the FPD. On the other hand, H_2S was determined at levels up to 100 ppm, demonstrating a dynamic range somewhat larger than the FPD. Like other polarographic detectors, this detector also responds to other oxidizable gases such as NO, CO, SO_2, and NO_2 and can be used for their determination if adequate separations are first achieved. Although the system described by Stetter et al. required up to 10 injections of H_2S before the response stabilized, reproducibility then remained stable (± 2.5% RSD) for up to eight hours. Other advantages of the polarographic detector are the freedom from reagent requirements and general convenience of use.

However, several major disadvantages are also apparent. Response time is slow, causing peaks to tail for approximately a minute, behavior which is unacceptable especially for WCOT or capillary columns. The detector response depends on molecular form, so that each gas must be calibrated separately. Thus, it is not clear whether mercaptans, COS, or other stable forms of organic sulfur can be detected.

The electrolytic conductivity detector (CD) operates by combusting or hydrogenating the sample, scrubbing interfering gases, bubbling the combustion gas through a solvent such as water, and measuring the change in electrical conductivity. Natusch and Thorpe (1973) and Hall both review the operating principles of such detectors, and Schiller and Brovsky (1977) discuss their application to the measurement of S gases in hydrocarbon matrices. According to the latter authors, detectability with the CD is approximately 10^{-9}g for S, poorer than the FPD but certainly adequate for retort gas.

Advantages of the CD over the FPD for retort gas include a higher dynamic range, a linear response to S, and less severe interferences due to hydrocarbons. On the other hand, the operation of the CD is less convenient than the FPD, requiring reagents, solvent pumps and circulating fluids, an ion exchange bed, and a gas/liquid scrubber. The time response is poorer than the FPD, and the chromatograms shown by Schiller exhibit tailing for approximately a minute. Ideally, if all S species were converted quantitatively to the same form (e.g. SO_2), the response of the CD should be independent of molecular form. In practice the combustion efficiency depends on the chemical form of S, and the response of the CD is determined by furnace temperature, the solvent and carrier gas flow rates, the molecular form of S, and the flow rate of the solvent. Each chemical form of S thus requires separate standardization. Although either oxidation or hydrogeneration can be completed in the reactors, Schiller et al. found that for the analysis of hydrocarbon mixtures a stable baseline could be achieved only in the oxidation mode.

In summary, the CD appears to be a promising detector for retort gases. Although the response time is not suitable for high resolution columns, its superior freedom from hydrocarbon interferences makes this less of a problem than for the FPD. Its higher dynamic range is more suitable than the FPD for retort gas. The principal disadvantage of the CD is its rather complex circulating and cleaning system and the associated time lag and inconvenience of operation, especially under field conditions.

The photoionization detector (PID) operates by exposing the eluting gases to a UV (e.g. 10.2 eV) light source and measuring the induced photoelectric current. Therefore they detect any compound with a sufficiently low work function rather than specific elements. Advantages of the PID include lack of fuel requirements, a linear range of 10^6 compared to 10^3 for the FPD, ease of operation, and low cost (Smith and Krause, 1978). Disadvantages include the lack of selectivity and compound-dependent sensitivity.

Smith and Krause (1978) report on the application of the PID to the determination of CS_2 in the industrial atmosphere. These authors report a range of 0.001- 50,000 ng for CS_2. However, the PID has clearly not found wide application in pollution measurements.

The microcoulometric detector (MCD) has also found limited application for the selective measurement of S compounds in complex mixtures. These systems operate by combusting or hydrogenerating the effluent stream, scrubbing interfering gases, and titrating the final product coulometrically. (See Wallace et al. [1970] and Martin and Grant [1965] for more complete descriptions.) For S compounds in petroleum products Martin and Grant report an operating range of 10^{-8} - 10^{-5} g. Special advantages of the MCD includes stable calibration and response to all S compounds. Disadvantages include complex instrumentation, reagent requirements, sensitivity to flow and reactor conditions, and poor time resolution.

4.4.4 Applications

Skogen (1980) has regularly used gas chromatography with flame photometric detection (Hewlett Packard Model 5700/5710) since 1976 to monitor gaseous sulfur species at Occidental Oil Shale, Inc. modified in situ retorts. A sample splitter using ratios between 1:1 to 1:5 has been used in conjunction with a 1/8 ml sample loop to monitor H_2S in the range of 100 ppm to 3000 ppm. Both polyphenylether and a 6' x 1/8" diameter Teflon column packed with 5% QF-1 on 80-100 mesh Poropak QS have been used as columns. The latter is preferred due to better peak separation and less tailing. Temperature programming starts at 65°C and increases to 140°C at a rate of 8° per minute.

Skogen reports that this system is operated in a mine and has proven reliable under severe environmental conditions. These conditions included shocks from blasting, dust, and control room temperatures up to 100°F. Water and oil are removed from the sample by traps and filters.

A operational difficulty is finding sample loops small enough to accomodate the low dymanic range of the flame photometric detector. The analyses of direct process gases, which are typically at least ten times more concentrated in H_2S, may therefore require a less sensitive detector or a smaller sample injection system.

At the Oil Shale Symposium: Sampling, Analysis, and Quality Assurance (March, 1979), Gangwal reported on a sampling and analysis scheme for measuring H_2S, COS, SO_2, CH_3SH, C_2H_6S, CS_2, and thiophene using a Porapak N column and a dual flame FPD. With coal gas, H_2S and COS were only partially separated. Even using the dual flame detector, most gases required separate calibration, although H_2S, COS, and SO_2 collapsed onto a single calibration curve when plotted against $A/\sqrt{h}$, where A is the peak area and h is the peak height.

Gangwal's data clearly indicated the virtue of the dual flame FPD. With the single flame detector the response to CH_3SH, C_2H_6S, and CS_2 varied by 75% due to hydrocarbons co-eluting from previous injections.

In summary, field experience has provided data on the reliability and operational problems associated with several manual and instrumental techniques. However, data on the accuracy and precision of the methods are not available. Establishment of these parameters will require the analysis of known samples and the simultaneous analysis of the same gas stream by several techniques.

4.5 Additional Spectral Techniques

Spectral techniques are attractive for the analysis of retort gases for two primary reasons. First, in situ measurements are at least theoretically possible, thereby avoiding sample conditioning (and alteration). Second, several gas components may be measured simultaneously. This could yield dividends in the form of better diagnostics and controls for both the retorting and pollution control operations.

Spectral techniques are obviously widely used for monitoring criteria pollutants such as SO_2 and NO_x, but most commercial instruments for this purpose are limited to a single species (e.g. UV fluorescence for SO_2). Similarly, techniques such as IR spectrometry are obviously widely used in the laboratory for in situ analysis of multi-component mixtures. However, the application of such approaches to the analyses of retort gas is not widespread and is essentially absent from the literature.

This section will therefore briefly review the possibility of applying techniques such as microwave and UV spectroscopy to the multicomponent analysis of retort gases. The literature on any one of these techniques is large, and I make no effort to review the entire subject here but attempt only to highlight those features especially relevant to the analyses of retort gas.

4.5.1 Second Derivative Spectroscopy

Two principal types of second derivative spectrometers are described in the literature: those which scan the absorption spectrum with time and then calculate the various derivatives, and those which obtain the second derivative directly as an electronic signal from the photomultiplier. The latter spectrometers operate by modulating the incident wavelength sinusoidally about the absorption peak maxima, and recording the second harmonic from the detector (Hager, 1973; Cahill, 1979).

In comparison to the more common spectrometers which measure optical absorption, optically modulated second derivative spectrometers (OMDS) often exhibit a signal-to-noise ratio which is improved several orders of magnitude, and are therefore attractive for the detection of trace components. On the other hand, electronic derivative spectrometers produce quite the opposite effect and will not be discussed further in this report.

The OMDS produces a signal S which is related to the concentration by equation 4.2 (Hager, 1973).

$$C = -\frac{S}{I} \cdot \frac{4}{(\Delta\lambda)^2} \cdot \frac{1}{\ell} \cdot \frac{1}{(d^2a/d\lambda^2)} \qquad (4.2)$$

where C = concentration of analyte

S = the second harmonic signal

I = the average intensity of the signal

λ = wavelength

$\Delta\lambda$ = the wavelength modulation amplitude

ℓ = absorption path length

a = absorbance of the analyte

In this equation, the first four terms are under the control of the operator and instrument designer, and the last term is a physical characteristic of the molecule.

Three features are of particular interest in this equation. First, OMDS clearly favors the detection of those species with sharp absorption lines, typical of simple inorganic molecules, while discriminating against broadband absorption. Thus, OMDS provides a means of compensating for background due to broad-band absorption and scattering. Second, unlike normal absorption spectrometers where concentration is related logarithmically to intensity, OMSD signal is related linearly to intensity. This feature favors a wider dynamic range. Third, the OMSD technique is relatively insensitive to drift in the light source and associated electronics, since S and I are both measured at the same phototube. Unlike other techniques designed to compensate for background absorption, the OMSD spectrometer has only one light source, one optical path, and one photo-detector.

OMSD spectrometers normally operate in the UV region in order to take advantage of the higher absorption coefficients in this part of the spectrum. At these wavelengths matrix gases such as N_2, O_2, H_2, and H_2O do not absorb, so that sample modification is not required. This feature is particularly attractive for retort gases where removal of water may inadvertantly remove other soluble gases such as CO_2, NH_3, H_2S, and SO_2.

Aside from these general comments, I am unaware of any studies detailing the application of OMSD spectroscopy to retort gas. Clearly, the availability of interference-free spectral windows and sufficiently sharp spectral lines should be one of the first areas of investigation. Table 4.9 lists interference-free detection limits for a few gases as measured by OMSD spectroscopy. While these numbers are encouraging for NH_3, NO, NO_2, SO_2, and Hg vapor, the feasibility of measuring these compounds in retort gas must still be determined experimentally.

TABLE 4.9. DETECTION LIMITS FOR VARIOUS GASES BY SECOND DERIVATIVE SPECTROSCOPY (Hager, 1973)

Compound	ppb(v/v)
NO	5
NO_2	40
SO_2	1
O_3	40
NH_3	1
Benzene	25
Toluene	50
Xylene	100
Styrene	100
Formaldehyde	200
Mercury Vapor	0.5

4.5.2 Millimeter Wave Spectroscopy

Microwave rotational spectroscopy can serve as a specific and sensitive tool for monitoring gaseous constituents in the environment and also for controlling gas treatment technology (Hrubesh, 1973; Kolbe et al., 1977; Leskovar and Kolbe, 1978). The physical process leading to absorption is the coupling of incident microwave radiation with the permanent dipole moment of a rotating molecule.

The advantages of microwave rotational spectroscopy as a technique for gas detection and measurement include the following:

- Spectra can be measured with a high frequency resolution of one part in 10^5 to 10^6. Thus, the measurement of a single line usually permits the determination of a constituent in a mixture.
- A single instrument can be used to monitor a number of constituents by automatic tuning of the frequency.
- Recent progress in mm wave technology permits the development of portable, all solid-state, spectroscopic instruments.

The peak value of the gas absorption coefficient can be approximated by

$$p = A\nu^2 \qquad (4.3)$$

where A is a quantity which depends on such gas parameters as concentration, pressure, temperature, rotational transition mode and fraction of the molecules in the transition state of interest. The frequency of peak absorption is ν (Gordy and Cook, 1970).

Since the absorption coefficients of typical molecules are small ($\gamma \cong 7 \times 10^6$ cm^{-1} for SO_2 at 20 GHz) and are also proportional to ν^2, it is important to select rotational transition modes at frequencies as high as possible. At higher frequencies there is also a larger thermal population difference, which helps to increase the quantity A in equation (4.3) and thus the absorption coefficient.

Because of the small absorption coefficients and because saturation occurs at relatively small drive powers P (=1w), a highly sensitive detector is required. Up to now the unavailability of lockable, solid-state oscillators and sensitive detectors has restricted the operation of such mm wave spectrometers to frequencies below about 80 GHz (Zoellner et al., 1979). Recently, work has been initiated to raise this upper frequency limit to 145 GHz using specially designed upconverters (Edrich, 1979) and improved mixing techniques with higher efficiencies (Carlson et al., 1978; Edrich et al., 1978; Kerr, 1979; Edrich, 1979). These improvements are expected to lead to (a) higher detection sensitivity and selectivity, and (b) to coverage of more line frequencies, (more molecular species with one single spectrometer).

At the present time a major disadvantage to microwave spectroscopy is the lack of adequate commercially-available equipment. However, the recent advances discussed in the previous paragraph auger well for the wider application of this technique.

A spectrometer covering the two bands 69.5 ± 3.5 GHz and 23 ± 1.5 GHz could detect several important gas components (Table 4.10) based on the occurrence of spectral lines in these regions and could be constructed with technology and components. Such components would include a single locked rf source with improved noise characteristics and a high-Q Fabry Perot microwave resonator with improved multispectral coupling and filter characteristics. This instrument could, for example, measure SO_2 concentrations down to 1 ppm using a time constant of 1 sec. Table 4.10 lists a number of pertinent molecules and their transition frequencies, which would be covered by such an instrument.

TABLE 4.10. VARIOUS GASES DETECTABLE BY A DUAL-WAVELENGTH MILLIMETER WAVE SPECTROMETER

Molecule	MHz Frequency
$C^{12}\ H_3\ S^{32}\ H$	21,973.2
$H\ N^{14}\ C^{12}\ O^{16}$	21,981.7
H_2O^{16}	22,235.1
$N^{14}\ H_3$	23,098.8
SO	66,039.9
$O^{16}\ O^{18}\ O^{18}$	22,527.0
$S^{32}\ O_2^{16}$	22,482.5
$N^{14}\ O_2^{16}$	70,589.7
$H_2\ C^{12}\ O^{16}$	72,409.1
$O^{16}\ C^{12}\ S^{32}$	72,976.8

4.5.3 Mass Spectrometry

Although mass spectrometry is not an in situ technique, as are the other methods discussed in this section, it is included at this point because of its ability to determine multiple species in a complex mixture. Because the mass spectrometer operates under vacuum, the sample stream not only must be diluted but typically must also be dried and scrubbed of corrosive gases in order to prevent damage to the high-vacuum components.

Advantages of mass spectrometry include the ability to monitor several species with a high degree of specificity and flexibility on a continuous, real-time basis by monitoring a corresponding set of mass-to-charge ratios. The list of monitored gases can be easily changed by programming a different set of peaks. Of course, this simple-minded approach assumes the availability of interference-free peaks, an assumption that has not yet been verified for retort gas.

One of the principal disadvantages of mass spectrometry is the lack of commercially available, inexpensive, and sufficiently rugged mass spectrometers for field use. Laboratory mass spectrometers are usually expensive and require considerable skilled maintenance. High-vacuum materials are normally incompatible with corrosive gases and high levels of water vapor. The availability of an inexpensive, low maintenance, rugged mass spectrometer would thus appear essential before the application of mass spectrometry to process streams could become routine.

4.5.4 UV and IR Absorption

UV and IR absorption is obviously widely used in both laboratory and field conditions for in situ analyses, and several of the stack gas monitors shown in Table 4.4 operate on the principal of UV or IR absorption. However, such instruments are typically optimized for a single species, such as SO_2, and cannot serve as multiple-species detectors. Among the instruments listed in Table 4.4, only the Wilks Scientific instrument--which is actually designed for industrial hygiene purposes--is tunable to different gases, and it is not clear whether this instrument can be used without modification for retort gas analysis.

In my experience, UV and IR absorption methods have not been thoroughly tested for the in-line analysis of retort gas, and several questions must be addressed prior to their widespread use. The existing monitors for criteria gases are primarily designed and tested for ambient air or thoroughly combusted stack gases. What additional spectral interferences occur in retort gas? To what degree can absorptive methods be extended to additional species such as NH_3, CHN, mercaptans, COS, and other gases of potential interest? Although absorptive techniques in theory operate in situ, in practice sample streams are often dried and cooled in order to protect optical components. Does such pretreatment alter the composition of retort gas, or can instrument optics be modified to tolerate untreated retort gas?

4.6 Mercury

This section treats the measurement of trace metals (especially Hg) in the gas phase while trace metals in solids and liquids are treated in Chapter 2. Since any number of techniques are available once the sample is collected, the emphasis here is on the sampling technique unless the monitor is used to detect Hg on-line in the gas phase.

4.6.1 Methods

Table 4.11 summarizes methods which are available for sampling and analyzing mercury vapor. As can be seen, most of the methods are designed primarily for ambient air or the industrial workplace. However, these methods may often be adapted to waste streams through the judicious use of sorbents or combustors and scrubbers upstream from the mercury collector.

The sampling techniques in Table 4.11 can be roughly categorized into groups:

(1) Aqueous solutions of stabilizing reagents, the most popular being ICl, HNO_3, and acidic $KMnO_4$

(2) Solid adsorbents, such as MnO_2 and activated carbon

(3) Au or Ag wool amalgamation cartridges

In addition, the on-line Zeeman atomic absorption (ZAA) analyzer requires no sample collection but rather detects Hg vapor directly in the gas phase.

Driscoll (1977) briefly reviews the major advantages and disadvantages of the common methods of sampling stationary sources for Hg, and the reader is referred to that source for a more detailed description.

TABLE 4.11. METHODS FOR COLLECTING AND MEASURING MERCURY VAPOR

General Methods	
Collection on Au/quartz wool; hydrocarbon streams and air	Ohkawa and Kondo (1977)
Collection with $KMnO_4/H_2SO_4$ solution; air	Gardner (1976); Hara (1975)
Collection on carbon-loaded filter paper; industrial atmospheres	Janssen et al. (1976)
Collection on MnO_2; industrial atmospheres	Janssen et al. (1977)
Piezo-electric Hg monitor for industrial hygiene	Scheide and Warnar (1978)
Collection on hopcalite; industrial atmospheres	McCullen and Michaud (1978)
Review of sampling methods for stationary sources: Absorption, amalgamation, and solid sorbents	Driscoll (1977)
Collection on Ag wool; industrial environment	Kneip (1975)
Zeeman atomic absorption; on line measurement for retort gas	Girvin et al. (1979)
Molecular speciation through selective sorption	Braman and Johnson (1978)
Application to Retort gas	
Hg in product gas from simulated in situ retort; comparison of Zeeman atomic absorption and ICl absorption solutions	Fox et al. (1978) Fox et al. (1977)
Hg speciation through selective sorption at the Paraho retort; total Hg	Fruchter et al. (1979)
Hg evolution during Fisher assay	Donnell and Shaw (1977) Schendrikar & Faudel (1978)

The methods which appear most commonly in the literature are the Au amalgamation technique and ZAA spectrometry, and these deserve further discussion. While the former is widely practiced and commercial instruments are available for monitoring ambient air, the latter is still in the prototype stage and field-worthy models are currently being perfected. ICl absorption solutions have also been evaluated with respect to retort gas.

The principal advantages of the amalgamation techniques are the general ease of use and the pre-concentration factor obtained by passing a large volume of gas through a small mass of metal. However, Ag as an amalgamation metal is probably contraindicated because the ready formation of AgS with H_2S and other S gases, poisons the surface and reduces the collection efficiency (Driscoll, 1977). The principal advantage of Au is thus its lower reactivity and associated greater freedom from interferences.

Most applications of the Au amalgamation technique have been completed on thoroughly combusted gas streams, and adaptation to retort gas may require a combustor in-line prior to the amalgamator. While Au should be inert with regard to reactions with retort gases, condensation of hydrocarbons or water may readily degrade the collection efficiency.

A particular advantage of the Au amalgamation technique is its excellent detection limits. For example, suppose a nominal 1 CFM (typical of EPA method 5 sampling train) is passed through the amalgamator for one hour (Kalb, 1975). A typical detection limit for Hg using the standard flameless atomic absorption technique is conservatively 20 ng, thereby yielding a detection limit of approximately 10 ng/m^3 in the original gas stream. This figure compares with measurements of Hg in raw and burned retort gas which vary from 4 to 75 ug/m^3.

In addition to good detectability, other advantages of the Au amalgamation system include freedom from liquid solutions and relative freedom from interferences. Ohkawa and Kendo (1977) report that samples collected on Au wool are stable for 1 week at room temperature.

Disadvantages of amalgamation techniques include the possibility that the collection efficiency may be degraded by unsuspected condensates or adsorbents, and the limitation of measuring only elemental Hg. (An upstream combustor would also permit the measurement of total Hg.) Real time measurements are not possible, and time resolution much better than an hour seems unlikely. In addition, if the sample is injected directly from the Au amalgamator into the AA spectrometers, off-scale samples are irretrievably lost unless sample recovery or splitting is built into the system.

The design and operation of the ZAA spectrometer is explained by Girwin et al. (1979), Hadeishi (1972), and Miller and Koizumi (1979). As the name implies, ZAA spectrometry is unique in using Zeeman shifted lines to account for background correction. Because a single light source, optical path, and detector are employed, long term stability is superior to other AA spectrometers. Low frequency noise and changes in background absorption are accounted for by rapidly alternating between shifted and non-shifted lines.

The ZAA spectrometer described by Girwin et al. is being especially designed and optimized for the on-site monitoring of retort gas. In practice the sample is mixed with oxygen and burned prior to introduction into the optical absorption cell in order to minimize interferences and smoke formation. This technique therefore records total mercury content although gaseous elemental Hg might be tractable with an unheated cell. When operated in the field, the ZAA spectrometer exhibited a detection limit of approximately 20 $\mu g/m^3$ in the absence of background and approximately 100 $\mu g/m^3$ in the presence of 85% broadband extinction (Girwin and Hodson, 1979).

The unique advantage of the ZAA technique is the ability to monitor Hg on a real-time continuous basis. This is particularly important because Hg emission from an in situ retort may vary markedly during the course of a burn. Also important is the ability of the ZAA spectrometer to achieve background correction at levels up to 98% extinction, which permits the determination of free Hg in smoky and organic-laden gas streams. In addition, the ZAA avoids any question regarding sampling efficiency since the entire sample stream passes through the absorption cell.

One current disadvantage of ZAA spectrometry is the requirement for expensive, custom made instrumentation. Laboratory ZAA spectrometers have been available commercially only sporadically, and a change in this situation would increase the attractiveness of ZAA spectrometry. A field-worthy ZAA spectrometer is currently under development at LBL but is not yet commercially available. Although the ZAA spectrometer does achieve superior correction for broadband, molecular absorption and scattering, suppression and enhancement due to the presence of other chemicals remain a problem. Finally, the detectability of the ZAA technique is poorer than the Au amalgamation technique.

4.6.2 Applications

The attempts to collect Hg in retort gas using aqueous solutions illustrate the difficulty of this approach. For example, Shendrikar and Faudel (1978) attempted to measure the Hg mass balance during a Fischer assay using a HNO_3 solution to scrub Hg from the retort gas. Their results varied from 58% to 196% recovery, which may be explained in part by the loss of Hg to the condenser or other cooled parts (Donnell and Shaw, 1977). Fox et al. (1978) used a series of impingers containing ICl, NaOH, H_2O_2, and HNO_3 to collect Hg vapor in retort gas from a simulated in situ retort. Dark brown deposits were formed during sampling on the walls of the impingers, which had to be removed with an MIBK wash. Including the various bubbler solutions and washings, a total of seven media had to be analyzed for each sampling period. The majority of the Hg deposited in the brown precipitates rather than in the solutions, further complicating the procedure. In spite of this somewhat ardous approach, excellent agreement was seen with ZAA measurements (0.74 vs 0.71 ng/min) when the two methods were operated simultaneously.

The applications of the Au amalgamation technique is well illustrated by Fruchter et al., (1977) and Kalb (1975). Fruchter measured Hg vapor in the offgas from the chemical oxidizer and in the recycle gas at the Paraho retort. By measuring Hg in all other major process streams, he completed a reasonable Hg mass balance (84%) for the retort, a fact which speaks well for the Au amalgamation technique. Fruchter et al. also attempted to speciate both Hg and As through the application of the selective sorbents described in their paper.

Kolb (1975) measured Hg mass balances in a coal-fired utility. He recovered on the average 20% more Hg than expected in the flue gas, which is not significant considering the difficulties in representative sampling and analytical errors.

Fox et al. (1978) describe the application of an on-line ZAA spectrometer for the measurement of Hg in product gas from a simulated in situ retort at Laramie. They were able to detect Hg vapor on a continuous basis, and observed Hg eluting as a front as the burn neared completion. By measuring Hg in the raw and spent shale, retort water, oil, and retort gas, they completed a mass balance of 97%!

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5.0 QUALITY ASSURANCE

Quality assurance has been discussed extensively in the literature, including technical, legal, and management aspects. Although emphasis and technique may vary, quality assurance can be described and practiced in terms of the following six categories:

Personnel. Persons carrying out chemical analyses, sampling, and data handling should be adequately educated and experienced.

Instrumentation. The instruments should be appropriate for the type of measurement intended and should be carefully calibrated and maintained. Records of calibration should be readily available.

Methods. The methods of sampling, preservation, and chemical analysis should be thoroughly tested. For this reason standardized methods are often preferred when appropriate. The exact analytical method should be recorded for later reference.

Quality Control. Quality control--as opposed to quality assurance--refers to the application of statistical methods in the laboratory. The precision of each method should be determined as a function of concentration by repeating the analysis of a sufficient number of real samples. The accuracy should be established by analysis of standard reference materials, by participation in "round robin" studies, and by measurement of the recovery of analyte material which has been added to real samples. In routine assays, control charts may be used for detecting anomalous situations.

Record Keeping. Accurate records should be kept for all samples, including site, sampling techniques, preservation and shipment methods, date of receipt by the laboratory, the exact analytical method, and the raw data that was used to calculate the final value. Record keeping generally also includes maintaining permanent laboratory notebooks and archiving exact descriptions of the analytical methods used.

Management Structure. Quality assurance programs provide for an independent review process. In a research effort, reviews are typically undertaken by peers. In a routine testing laboratory or a forensic laboratory, technical reviews may be initiated by a quality assurance manager who reports independently of the laboratory manager. Materials of known composition may also be submitted by the quality assurance laboratory.

The details of such quality assurance programs have been treated by a number of organizations, including the Environmental Protection Agency (EPA), the American Society for Testing and Materials (ASTM), and the American Public Health Association (APHA). Mills (1979) provides an extensive list of references dealing with quality assurance. Books dealing more specifically with oil shale include Analytical Chemistry Pertaining to Oil Shale and Shale Oil, by Siggia and Uden (1974), Science and Technology of Oil Shale, by T.F. Yen (1976): and proceedings of the recent Oil Shale Symposium: Sampling, Analysis, and Quality Assurance, sponsored by the Denver Research Institute (1979). In addition, standard setting agencies and associations, including the EPA, ASTM, APHA, National Institute for Occupational Safety and Health (NIOSH), the Association of Official Analytical Chemists (AOAC) publish compendia of standardized analytical procedures.

The content of the previous chapters indicates clearly that the standard methods of chemical analysis and sampling, which are principally designed for routine testing laboratories, have not always been sufficient to assure the correct chemical analysis of oil shale wastes. This insufficiency arises primarily because the standardized methods of chemical analysis and sampling were not designed for oil shale wastes and must often be improved or entirely changed. Further, realistic standard materials must be developed for the analysis of oil shale wastes.

Analytical methods are discussed in the remaining sections in this report. In the next section I discuss the availability and importance of standard reference materials, as well as methods of sampling and sample preservation. In addition, because of the still undeveloped character of analytical methods for oil shale waste, and because of the reported difficulties in analyzing such materials, further quality assurance operations are recommended until procedures have been more thoroughly tested. These recommendations are described in the following sections of this chapter.

5.1 Standard Reference Materials

The ability of an individual laboratory to reproducibly analyze a complex sample often produces a false sense of confidence which is disrupted only when several laboratories analyze the same, homogenized sample. In such cases it is not unusual to find intra-laboratory precision on the order of a few percent while inter-laboratory differences may be larger than a factor of ten. This situation is amply illustrated by von Lehmden et al. (1974) for coal, fly ash, fuel, and gasoline. The availability of realistic samples of known composition is essential for revealing otherwise unsuspected analytical problems and for providing accurate standardization.

Table 5.1 provides a list of environmental standards which are currently used to evaluate the performance of an analytical method for environmental samples. Because only two of the standards are directly related to oil shale retorting, additional standards would be valuable.

The gas standards are simple mixtures in pure air or nitrogen, and are far removed from the hot, moist, hydrocarbon-based gases that are produced in oil shale retorting. A more realistic standard material for retort gas would therefore be an important contribution. Although the Laramie Energy Technology Center maintains a storage facility with a variety of product waters from oil shale retorting, to my knowledge only one has been characterized sufficiently to serve as a standard material. The water quality standards available from the EPA represent a far simpler matrix than would be encountered with realistic retort waters or leachates. Nevertheless, if a laboratory is unable to determine volatile organic compounds in pure water, it is unlikely they could do so in the unstable brines produced by oil shale retorting.

The standards materials in Table 5.1 represent a substantial advance in the ability of the analytical chemist to handle complex environmental samples. Nevertheless, for the purpose of oil shale retorting three types of standards are notably missing:

- Gas standards which simulate the wet, hot, hydrocarbon-based stream produced by oil shale retorting. Although standards for regulated gases such as SO_2, CO, and NO can be purchased (albeit in an unrealistically pure matrix), standards for trace metals in gases are entirely unavailable.

- Standards with known concentrations of organic materials.

- Solid samples for leaching studies. The main interest in solid waste is in the leachates which may be produced, and standardized leaching protocols clearly require the availability of a wide variety of solid waste with known leaching characteristics.

TABLE 5.1. STANDARD REFERENCE MATERIALS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES

Type of Sample	Species	Source/References
Coal, fly ash, fuel oil, water river sediment, urban particulate matter	trace elements	NBS (1979) Ondov et al. (1975) Greenburg (1979)
Criteria pollutants in air or N_2	O_2, SO_2, CO, NO, CO_2, CH_4, C_3H_8	NBS (1979)
Permeation tubes	SO_2, NO_2	NBS (1979)
Biological materials (orchard leaves, pine needles, bovine liver, etc.)	trace elements	NBS (1979)
Charcoal collection tubes	industrial solvents	NBS (1979)
Oils (Conostan)	trace metals	Continental Oil
Water	turbidity	Amco

TABLE 5.1 (continued)

Type of Sample	Species	Source/References
Water (surface or drinking quality)	trace metals, nutrients, minerals, BOD, TOC, COD, inorganic ions, soluble and volatile organic compounds, suspended solids, petroleum hydrocarbons	EPA
Various product waters associated with oil shale retorting	trace metals and various water quality parameters	Laramie Energy Technology Center (DOE) Fox et al. (9178) Farrier et al. (1977)
Raw and spent oil shale	47 elements	Fox et al. (1979)
Various minerals	major, minor, and trace elements	USGS Flanagan (1976)
Pure compounds	priority (consent degree) pollutants	See EPA (1977) for list of sources

Because of the shortage of adequate standards and sufficiently developed analytical techniques, I recommend that the analyst include, whenever possible, the following quality assurance guidelines in addition to the practices normally recommended by standard setting agencies:

- For selected samples, each species should be determined by more than one independent technique (whenever possible). The results of both techniques should be reported.

- At least one standard reference material should be analyzed with the samples of interest and the results included in the final report.

- The precision of the method should be experimentally determined for each study by repeating the analysis of a sufficient number of samples. Handbooks of standard methods, such as those published by the Environmental Protection Agency and the American Public Health Association often include descriptions of typical measurement errors. However, these should not be relied upon for oil shale waste products.

- Known amounts of analyte should be added to selected samples and the recovery should be measured, as is typical practice with routine analysis. However, this recovery should also be included in the final report.

5.2 The Collection and Preservation of Solids and Liquid Samples

This section specifically excludes the collection and preservation of normal ground waters and surface waters. Also the collection and storage of gaseous samples is treated elsewhere, in Chapter 4. This chapter deals with solids and wastewaters, including methods of collection, preservation techniques, and to a limited extent their preparation for analysis (e.g. the filtering of wastewaters).

Standardized procedures for the collection and preservation of normal ground and surface waters and solid materials have been developed by several government and standard setting agencies. These include the Environmental Protection Agency (EPA), the United States Geological Survey (USGS), the American Society for Testing Materials (ASTM), the American Public Health Association (APHA), and the Association of Official Analytical Chemists (AOAC). The EPA has published guidelines specifically for sampling and preserving water and wastewater (1976, 1977). They are also developing standardized protocols for collecting and leaching solid waste for the purpose of defining hazardous materials. The USGS publishes a series of guidelines titled, "Techniques of Water Resource Investigations of the United States Geological Survey." An example of an item from this series is Wood's (1976) "Guidelines for Collection and Field Analysis of Ground Water Samples for Selected Unstable Constituents." The EPA is also preparing a "Pollution Control Guidance Document for Oil Shale Development" (in press), which summarizes many of the standardized techniques which are available. These documents, though not necessarily sufficient for oil shale wastes, form a valid basis for further investigation.

Obtaining a representative sample of a granular solid is a basic problem in analytical chemistry and is not unique to oil shale waste. Statistical theories have been developed which relate particle size, density, analyte concentration, and sampling variance. (See, for example, Laitinen [1960].) Such theories usually begin by postulating the existence of two types of particles: those that contain the analyte of interest as a pure compound, and those that contain the carrier material. Such approaches also assume a monodisperse size distribution of particles. Simple binomial theory is then used to relate the number of analyte particles required for a preselected maximum variance, and the minimum sample size follows immediately.

Harris and Kratochvil (1974) and Harris (1978) have developed similar statistical theories of the minimum sample size. However, they permitted the analyte to be distributed in two different types of particles and then described the minimum sample that is required for a given sampling variance as a function of particle diameter, density, and the distribution of the analyte between particles. Carley (1979) discusses the application of statistical theory to the sampling of oil shale and spent shale. As he points out, such samples are never monodisperse in diameter and quite likely do not contain the analyte as distinct particles. He addresses this problem by developing a statistical theory for the sampling of granular solids with a continuous size distribution.

The contamination of solid samples by trace metals during sample grinding and sieving is another common problem of the analyst. Sample contamination is discussed by Meyers and Burnett (1953) and Thompson and Bankston (1970).

Other references are available for the analyst interested in sampling and sample preservation. For example, Maienthal and Becker (1976) review sample handling and preservation of environmental samples. La Fleur (1976) discusses accuracy in trace analysis including sampling, sample handling, and analysis. Carter also provides a bibliography of methods for the preservation of wastewater samples, which is included at the end of this chapter.

5.2.1 Relevance to Oil Shale

Although the above mentioned references may provide general guidelines for sampling and preservation, no sampling or preservation techniques can be applicable to all samples. This fact is illustrated by

Carter, (1979) who experimentally determined holding times for species in a variety of industrial waste waters. Table 5.2 compares the holding times experimentally established by Carter with those recommended in the EPA handbook, "Methods for Chemical Analysis of Water and Waste". Table 5.2 also lists the preservatives recommended by Carter which are normally, but not always, recommended by the EPA handbook.

The experimentally established holding times shown in Table 5.2, column 3, are normally considerably longer than those recommended by the EPA handbook, with the exception of pH and Hg. Since sample holding times can be a major factor affecting the cost of a project, for industrial effluents strict adherence to the EPA holding times would result in dramatically increased cost as well as compromised data on pH and Hg.

Clearly, generalized holding times which are recommended in the literature are neither sufficient nor necessary for the purposes of monitoring process waters from oil shale retorting. For example, process waters would often be exposed to partial pressures of CO_2 and H_2S which are elevated above atmospheric partial pressures of these gases and may therefore lose HCO_3^- and HS^- rapidly upon standing.

I therefore recommend, especially for crucial parameters, that holding times be established experimentally for the process waters under study. This could be done, for example, by preparing sealed vials containing known levels of contaminants, the contents of which could be added to duplicate samples when they are collected in the field. Recovery in the laboratory of said additions would then suggest adequate preservation.

In the spirit of this recommendation, the rest of this chapter deals specifically with the sampling and preservation of oil shale wastes. The reader is also referred to Wildeman's (1979) review of oil shale sampling. In the remainder of the chapter practical experience gained through field operations, collection of solid samples, and collection, preservation, and treatment of waste water samples are discussed.

TABLE 5.2 EPA RECOMMENDED HOLDING TIMES COMPARED TO EXPERIMENTALLY ESTABLISHED HOLDING TIMES (Carter, 1979; EPA, 1979)

	Experimentally Established for a Variety of Industrial Wastewaters		Listed in EPA** Methods Manual
Measurement	Preservative	Holding Time	Holding Time
Alkalinity	4°C	2 wks	24 hrs
BOD	4°C	48 hrs	6 hrs
Bromide	none req.	4 wks	24 hrs
COD	4°C, H_2SO_4 to pH<2	4 wks	7 days
Chloride	none req.	4 wks	7 days
Cyanides	4°C, NaOH to pH>12	2 wks	24 hrs
Fluoride	none req.	4 wks	7 days
Hardness	HNO_3 to pH>2	6 mos	7 days
Iodide	store in dark	4 wks	24 hrs
Mercury	0.05% $K_2Cr_2O_7$, HNO_3 to pH<2	4 wks	38 days
Nitrogen			
Ammonia	4°C, H_2SO_4 to pH<2	4 wks	24 hrs
Kjeldahl	4°C, H_2SO_4 to pH<2	4 wks	24 hrs
Nitrate + Nitrite	4°C, H_2SO_4 to pH<2	4 wks	24 hrs
Nitrite	4°C 4°C, 800 mg/l $HgCl_2$	24 hrs 7 days	24 hrs --
Oil & Grease	4°C, H_2SO_4 to pH<2	4 wks	24 hrs
Organic Carbon	4°C, H_2SO_4 to ph<2	4 wks	24 hrs
pH	4°C	1 hr*	6 hrs
Phenolics	4°C, H_2SO_4 to pH<2	4 wks	24 hrs

TABLE 5.2 (continued)

Measurement	Experimentally Established for a Variety of Industrial Wastewaters Preservative	Holding Time	Listed in EPA Methods Manual** Holding Time
Phosphorus			
Orthophosphate Dissolved	4°C	24 hrs	24 hrs
	4°C, 800 mg/l $HgCl_2$	7 days	--
Hydrolyzable	4°C	24 hrs	24 hrs
	4°C, 800 mg/l $HgCl_2$	7 days	--
Total	4°C, H_2SO_4 to pH<2	4 wks	24 hrs
Total Dissolved	4°C, H_2SO_4 to pH<2	4 wks	24 hrs
Residual Chlorine	4°C	1 hr	--
Residue			
Filterable	4°C	2 wks	7 days
Nonfilterable	4°C	1 wk	7 days
Total	4°C	2 wks	7 days
Silica	4°C	4 wks	7 days
Specific Conductance	4°C	4 wks	24 hrs
Sulfate	4°C	4 wks	7 days
Sulfide	4°C, 2 ml zinc acetate	1 wk	24 hrs
Turbidity	4°C	24 hrs	7 days

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*For accuracy of 0.2 pH units, two weeks holding time otherwise.
**From EPA methods for chemical analysis of water and wastes.

Before beginning an extensive laboratory study of sampling or preservation, analysts should be aware of the practical sampling problems encountered in the field. It is indeed perplexing to spend six months in the laboratory refining techniques for preserving zinc and copper in retort waters only to find upon arrival at the retort site that all plumbing is in brass and copper, and that all process waters are therefore badly contaminated with these elements. The reader is referred to several reports which detail the practical problems of sample collection. Farrier et al. (1977), for example, describe the collection, homogenization, and preservation of retort waters from the true in situ retort number nine at Green River. Prien et al. (1977) and Cotter et al. (1977) describe their sampling strategy and problems at the Paraho retort near Rifle. Prien and Cotter made several recommendations for future programs, ranging from the proper sampling probes and access portals to the use of a portable on site gas chromatograph. Fox et al. (1978) discuss the collection of retort waters for trace element analysis. Wildeman (1979) and Bonomo (1974) should be consulted for additional descriptions of practical sampling problems.

Much of the effort in obtaining representative samples of raw and spent shale is related to the determination of mass balances and the prediction of oil yield. Since the raw shale fed to the retort may vary in diameter from a few micrometers to several inches, obtaining a representative sample is important. Wildeman and Hiestand (1979) describe the automated sampling system for the Paraho retort, which collects 200 lbs of material on a preset schedule, and then successively splits and grinds the sample to -¼ inch. This sampler has been shown to be adequate for predicting oil yield in the plant as well as trace element content.

Using this automated sampler Wildeman (1979) and Wildeman and Hiestand (1979) have completed an extensive analysis of variance for the errors associated with sampling for seventeen trace metals, and for Fischer assay oil yield. They found that over a thirty day period the content for most trace elements varied less than a factor of 2, compared with a ten-fold variation observed in most geological deposits. This variance indicates that the distribution of trace elements in oil shale is unusually consistent. Wildeman and Hiestand collected samples on an hourly, 8-hourly, and daily basis and assigned the overall variance to sampling and analytical uncertainties. For most trace elements the analysis variance was greater than the sampling variance. These authors concluded that for a thirty day operation composite samples could be collected weekly for the purpose of determining trace element balances.

The situation for Fischer assay oil yield, and hence the content of organic compounds, is quite different. These same authors found that the day-to-day variations in the oil shale quality were larger than any other measurement error. They concluded that for determining oil yield, daily composite samples were recommended but hourly samples were unnecessary.

Of course, once a -¼ inch sample is received from the plant site further size reduction must occur prior to most analyses. Wildeman and Meglen (1978) described their experience in crushing and grinding raw oil shale from the Paraho retort. They could easily crush the sample to -10 mesh, although further size reduction was difficult because of the resinous nature of the oil shale particles. In addition, levels of Co, Cu, Zn, and Pb in oil shale are low enough that contamination can possibly arise from normal sieving and grinding operations. For this reason Wildeman and Meglen recommend that no sieves or disc pulverizers be used. They used instead a shatter box and recommend only hardened steel or tungsten carbide surfaces. For the same purposes, Fruchter et al. (1979) used alumina jar mills, blended samples in polyethylene mixers, and subdivided their samples with a riffle splitter.

Once size reduction is complete, many analytical schemes then require sample destruction in a basic molten salt or digestion or extraction in strong acid. Wildeman and Meglen (1978) have studied this problem in relationship to the Paraho program. They found that the typical basic salt fusion was complicated by the presence of organic matter which would evaporate or burn before the flux would melt--a situation favorable for the escape of the more volatile trace elements. They therefore recommended the use of low melting point fluxes. Digestion with strong acids did achieve 90-95% extraction of As and Se, but required very meticulous technique. In concluding they recommended a Na_2CO_3 flux in platinum crucibles for the determination of major elements and boron. A $LiBO_2$ flux was also evaluated and performed adequately. A Na_2O_2 flux in a Zr crucible was recommended for the determination of Se and As. Finally, samples requiring F analysis were decomposed in a NaOH flux in a Ni crucible. In situations where samples were not decomposed but only ground finely prior to analysis, Wildeman and Meglen (1978) found that Rb and Sr were homogeneous to a level of 300 micrograms within the error of the analytical technique. For further information on decomposition techniques the reader is referred to The Destruction of Organic Matter, by Gorsuch (1970) and Decomposition Techniques in Inorganic Analysis, by Dolezal et al. (1966).

The determination of Hg in spent retorted shale presents an unusual and interesting problem. A number of investigators have attempted to measure Hg balances in Fischer assay and in pilot scale plant operation, but were often unsuccessful. Typically a net loss of mercury occurred during retorting, which was ascribed to the volatilization and escape of mercury vapors, a hypothesis which could not be confirmed until the Hg leaving with the retort gas could be measured. Occasionally a positive net increase in mercury was measured, suggesting a sampling error. In 1978, Fox et al. confirmed that mercury in fact did elute with the final volumes of retort gas. More importantly, from the view point of sampling the spent shale, the Hg was shown to move in a band ahead of the combustion zone in a simulated in situ retort. The mercury, upon evaporating, apparently condenses on the cooler shale ahead of the combustion front, or in some cases on any cooler surface. Thus, unlike trace metals in most minerals, Hg in spent shale is distributed in a nonrandom manner, violating the first assumptions upon which most sampling strategies are based, and requiring an unusual amount of diligence in obtaining representative samples.

In contrast to solids, representative wastewaters samples can usually be collected more easily. However, unlike most mineral samples, wastewater samples are subject to chemical and physical changes due to bacterial actions, the release of dissolved gases, and chemical reactions which may proceed for months after the sample is collected. Thus the difficulty of obtaining a representative sample should not be overlooked. The wastewater sample may be stratified or present as a water-oil emulsion. Discharge quantity may change abruptly due to normal plant operations, upset conditions, or cleaning operations. In addition, from an in situ or modified in situ retorting procedure the wastewater quality changes dramatically between the start and finish of the operation.

The omega-9 wastewaters from the Green River burn number 9 (Farrier et al., 1977) have been most thoroughly studied with regard to sample collection, preservation, and handling. As the authors note, this wastewater may be somewhat atypical of most retort waters because of a heavy contribution of ground water; nevertheless, much of what is known about handling retort waters has been established through the availability of these samples, and their sampling experience is well worth recounting.

Farrier et al. (1977) first collected the samples in a pond near the retort. They observed a turbidity in the sample which could be removed only by filtering through a 0.45 micrometer membrane filter. Other techniques for removing suspended particulate matter, such as high speed centrifugation and filtering through coarser filters, were unsuccessful. In addition to removing suspended oil droplets and minerals which could be present, filtering through the membrane effectively removed 99.99% of bacteria present. Much of the turbidity of this sample was eventually associated with active bacterial growth. The success of the filtering operation was judged by the production of a transparent liquid which was unobtainable by any other process they tried.

The clear filtrate produced in this manner was nevertheless unstable at room temperature, becoming turbid and forming an amorphous precipitate in a matter of days. Microscope examination of the particulate phase disclosed the presence of a prolific population of rod-shaped bacteria. These workers attempted to stabilize this retort water by purging with nitrogen, excluding light, increasing the pH, adding ethanol, and by storing at different temperatures. Of the combinations tested, filtering through a 0.45 micrometer filter and storing at 4°C was the only successful combination.

The development of turbidity in the omega-9 waters certainly leads one to expect changes in the organic content. Felix et al. (1977) confirmed this by using high pressure liquid chromatography with a ultraviolet detector. Chromatograms of waters stored at 4°C were different than those from waters stored at 37°C. Williams et al. (1979) monitored total dissolved organic carbon, total hydrophobic compounds, hydrophobic neutral compounds and pH in the omega-9 water as a function of time. In approximately two days he observed significant changes in pH, a 20% decrease in total dissolved organic carbon and total hydrophobic organic compounds, and a 60% decrease in hydrophobic neutral compounds.

Unlike many surface ground waters, the trace metal content of retort waters may not necessarily be preserved by acidification. A number of investigators, including Wildeman and Meglen (1978), have reported the formation of precipitates of sulfur and/or organic acids upon the addition of mineral acids. These reactions are not only likely to remove trace metals, but also to produce a generally messy sample.

In addition to the omega-9 waters, the preservation of waste waters from the Paraho process is discussed in the literature. Wildeman and Hoeffner (1979), for example, describe their efforts to preserve wastewaters from the Paraho process. Samples were placed in Teflon bottles and stored for approximately one year under the following regimes: 1) refrigerated, 2) purged with nitrogen and refrigerated, 3) frozen,

4) purged with nitrogen and frozen. Upon collection, Wildeman and Hoeffner measured pH and Eh; in addition to these two parameters, alkalinity, ammonia, thiosulfate, and total sulfur were measured upon opening the vials approximately one year later. During this period, pH values dropped slightly and Eh values increased significantly. The values of conductivity depended somewhat on the method of storage. The values for alkalinity, ammonia, thiosulfate, and total sulfur were approximately the same regardless of the storage technique, but no comparison to original values was possible. The consistency of values for total S and the major ions--HCO_3^-, NH_4^+, and thiosulfate--is somewhat suprising considering the changes in Eh and pH. Based on these experiments, the best method of sample storage cannot be selected because of the lack of adequate measurements at the time of sample collection.

In filtering certain retort waters, one also encounters difficulties not often seen in other wastewater samples. For example, some retort waters contain droplets of oil as a distinct phase which are not easily separated upon standing. Wildeman (1979) has found that filtering the sample through cotton adequately removes such oil.

Fox (1979) performed an interesting series of experiments on the effects of filtering eleven retort waters from the controlled state retort at the Laramie Energy Technology Center. As usual, she filtered the samples through a 0.45 micrometer pore diameter membrane filter to remove the particulate matter and thereby produced a clear solution. However, when these samples were immediately refiltered under vacuum, almost as much particulate mass was collected as during the first filtration! Closer examination revealed the growth of crystals on the filter paper ranging from 1 to 100 micrometers in diameter and containing elements such as calcium and magnesium. She proposed that calcium, magnesium, iron, and nickel were thus being removed as carbonates when the saturated solution of these elements was exposed to a vacuum. When solutions were allowed to stand for several days and become turbid through bacterial action, the elements Hg, Ni, Te, As, Br, and Se were also removed. This data suggests that these elements are somehow absorbed onto the bacterial debris which was removed by the filter.

5.2.2 Summary

Of the preservation methods discussed thus far for wastewaters, filtering with a 0.45 micrometer membrane filter and storing at 4°C has been shown to prevent obvious precipitation or the formation of turbidity. However, this evidence does not guarantee that other less obvious chemical changes are taking place. Is ammonia being lost? Are specific organic acids or bases changing? Indeed, are the preservation requirements of the omega-9 sample appropriate to other process waters?

Answers to these questions cannot be determined without further study and I therefore recommend that, especially for crucial parameters, holding times be established experimentally for the waters under consideration. This could be done, for example, by preparing sealed vials containing known levels of contaminants. Samples could then be collected in duplicate, the contents of a vial added to one sample container, and its contents added to duplicate samples in the field. Recovery in the laboratory of specified additions would then be one indication of adequate preservation.

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6.0 CONCLUSIONS

Of the methods discussed in the text, some have been evaluated for oil shale wastes and have been proven adequate; others have been proven inadequate and most have not yet been completely tested. It is therefore premature to recommend or require specific testing protocols as is done, for example, for ground and surface waters. As the summaries in the following paragraphs indicate, additional evaluation and development of analytical methods is still required.

Trace Elements

The status of analytical methods for trace elements in oil shale wastes is similar to that of most other complex samples. The total concentration of essentially every element can be determined by the proper combination of readily-available instrumental techniques such as neutron activation, X-ray fluorescence, spark source mass spectroscopy, inductively coupled plasma optical emission spectroscopy, traditional optical emission spectroscopy, and atomic absorption spectroscopy. As described in the text, for a specific sample and set of elements a combination of instrumental techniques can be selected by comparing their elemental coverage, accuracy, precision, and mode of operation.

Methods for trace elements in gas, such as Hg or As, are still under development.

Wastewaters

Of the species and physical characteristics discussed in the text, methods for determining pH, conductivity, F^-, NH_3, and NH_4^+ have been shown to be adequate for a limited number of wastewaters. Methods for Cl^-, total P, PO_4^{3-} total S, $SO_4^{=}$, $SO_3^{=}$, SCN^-, thiosulfate and other reduced sulfur oxides, CN^-, total N, and total dissolved solids are not confirmed. Methods for the latter species either lack confirmation by an independent method or have been shown to be inaccurate or inappropriate.

Gases

Burned flue gases from oil shale retorting should be similar in composition to utility and industrial sources which are already widely monitored for regulated gases such as SO_2 and NO_x. Existing monitors should therefore be appropriate for this application.

Methods for the analysis of product (retort) gas have not been widely investigated, presumably due to the difficulty of preparing standard gas mixtures similar in composition to the hot, moist gas produced by oil shale retorting. Gas chromatography and other techniques are promising, but still require further evaluation using known gas mixtures.

Quality Assurance

Wastewaters produced by oil shale retorting are biologically and chemically unstable. Based on a very limited number of samples, researchers have found filtering and cooling the wastewater the preferred method of preservation for many species.

For spent and raw shale, representative samples can be obtained for trace element analyses using normal splitting and blending procedures described in the text. Because of the low level of many trace elements in oil shale, sample grinding and handling may introduce significant contamination (See 5.2).

Standard reference materials are generally insufficient for most oil shale materials, although standard wastewater and shale samples are becoming more available. Standard retort gases are not available and will have to be generated in the laboratory.

7.0 RECOMMENDATIONS

Because laboratory study of every questionable analytical technique discussed in the text would not be feasible, I recommend that priority be given to evaluating methods which now seem essential to the development of pollution control technology, but which are not yet confirmed as valid. These include:

- Analysis of wastewaters for complex anion mixtures such as $S^{=}$, $S_2O_3^{2-}$, CN^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^-, and polythionates.

- Analysis of wastewaters for total nitrogen, total sulfur, total phosphorus, and total dissolved solutes.

- Analysis of retort gas for total sulfur and possible sulfur species, including H_2S, SO_2, COS, and mercaptans.

- Analysis of retort gas for possible N compounds, including NH_3, HCN, and NO_x.

While these methods are being validated in the laboratory, field programs must proceed using the best techniques presently available. However, the quality of analytical data from field work can be improved immediately by adopting the following guidelines, whenever possible, as standard procedures:

- Analytical accuracy should be established by determining species through more than one method and standard reference materials should be analyzed simultaneously with the samples. Recovery of analyte purposely added to the samples should be measured as another means of establishing accuracy.

- The precision of each method should be determined by repeating the analysis of selected samples. Statements of precision found in many compendia of standard methods usually apply only to ground and surface waters, and are inadequate for oil shale wastes.

- Decay of the various analytes in samples stored prior to analysis should be measured to determine how accurately the analyzed sample reflects the original concentration. Preservation techniques and safe storage times recommended by the various handbooks of standard methods are not applicable to oil shale wastes.

- Results of these three practices should be carefully recorded in the final report.

Applying these guidelines routinely will help assure the quality of analytical data. In addition, use of these guidelines will result in a confirming evaluation of analytical methods with a wider spectrum of samples and under more realistic conditions than could be expected in the laboratory. Methods which prove troublesome in the field should always be given the highest priorities for laboratory study.